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List of Acronyms and Abbreviations

ADNT	Aminodinitrotoluene
BRAC	Base realignment and closure
CO_2	Carbon Dioxide
CSU	Colorado State University
DNT	dinitrotoluene isomers
DNX	hexahydro – 1,3- dinitroso – 5- nitro-1,3,5 triazine
DoD	Department of Defense
DOE	Department of Energy
EPA	Environmental Protection Agency
ERDC	Engineer Research and Development Center
ESTCP	Environmental Security Technology Certification Program
GC/MS	Gas chromatography/mass spectrometry
H_2O_2	Hydrogen Peroxide
HMX	octahydro - 1,3,5,7 - tetranitro-1,3,5,7-tetrazine
HPLC- UV	High performance liquid chromatography – ultraviolet wavelength detector
IC	Ion chromatography
LSC	liquid scintillation counting
LC/MS	Liquid chromatography/mass spectrometry
MNX	hexahydro – 1- nitroso –3,5- dinitro-1,3,5 triazine
ORP	Oxidation reduction potential
PCD	Pueblo Chemical Depot
PQL	Practical Quantitation Limit
QA/QC	quality assurance/quality control
RDX	hexahydro-1,3,5-trinitiro-1,3,5-triazine
RPD	relative percent difference
SERDP	Strategic Environmental Research and Development Program
SHE	Standard hydrogen electrode
TAT	Triaminotoluene
TDS	Total Dissolved Solids
Ti-mmo	Titanium – mixed metal oxide
TNT	2,4,6-trinitrotoluene
TNX	hexahydro – 1,3,5 - trinitroso-1,3,5-triazine
USACE	United States Army Corps of Engineers

Acknowledgements

Executive Summary

In 2002, SERDP funded CSU to conduct proof of concept studies to evaluate sequential electrolytic degradation of energetic compounds using flow through electrolytic reactors (e⁻barriers). In 2003, SERDP provided supplemental funding for a more detailed analysis of reaction mechanisms and products. This report includes detailed results from these efforts.

The Phase 1 studies focused on proof of concept level experiments designed to evaluate the potential of an electrolytic approach for in-situ treatment of dissolved energetic compounds in groundwater. The technical approach was to first evaluate transformation potential using batch voltammetry experiments. Using information derived from the voltammetry experiments, flow-through soil columns were used to evaluate sequential electrolytic degradation of dissolved energetic compounds in a reactive barrier format.

The Phase 1 batch reactor studies indicated that energetic compounds can be degraded in electrolytic cells using expanded titanium-mixed metal oxide electrodes. The observed order of reactivity was 2,4-DNT>HMX>TNT>RDX. These studies also suggested that the threshold applied potential for degradation of TNT and RDX was approximately 7.5V.

For the flow-through reactor experiments, six identical flow-through electrolytic column reactors were packed with quartz feldspar sand to test treatment efficacy for TNT and RDX. Expanded titanium-mixed metal oxide electrodes spaced 2 cm apart were placed at the midpoint of the columns. The columns were intended to act as one-dimensional analogs for groundwater flow through an e⁻barrier. For each contaminant, one column was a no voltage control, one tested an oxidation-reduction sequence, and one tested a reduction-oxidation sequence. Studies were conducted using influent concentrations of 1,000 ug/L TNT and 500 ug/L RDX. Aqueous concentrations of TNT, RDX and reaction intermediates were determined using HPLC-UV and gas chromatography/mass spectrometry (GC/MS).

Analyses conducted using GC/MS indicated transformation of greater than 97% and 93% of the TNT and RDX, respectively, relative to the control, using the oxidation-reduction sequence. Removal greater than the cited value reflects concentrations lower than detectable levels. Replicate analyses using HPLC–UV indicated greater than 97% transformation for TNT and 98% transformation for RDX relative to the control reactors. Actual transformation may be greater due to analytical constraints. Common degradation intermediates were not observed using sequential oxidation-reduction. Transformation rates for TNT and RDX were lower in reactors testing sequential reduction-oxidation. In addition, the reduction-oxidation sequence produced detectable reaction intermediates.

Power requirements observed during the experiment suggest that high fractional transformation of TNT and RDX is possible with power densities in the range of

2-3 watt/m^2 of active electrode. Assuming \$0.05/kWh, this consumption corresponds to power costs of approximately \$0.002 – \$0.004/day/m^2 of active e$^-$barrier.

Phase 2 was initiated to provide additional insight into possible reaction mechanisms and to conduct mass balance studies. The technical approach of the Phase 2 work included batch and flow-through reactor studies. The batch reactors involved a single reaction vessel containing separate anode and cathode chambers of approximately 1 L each. A Nafion™ membrane separated the electrodes allowing independent study of processes at the anode and cathode. Results from the batch reactors indicated that cathodic reduction is the primary transformation mechanism for TNT and RDX. For TNT, cathodic reduction resulted in transformation levels of 99.8% at 4, 5, and 10V applied cell potential respectively and 80% transformation was observed at 3V cell potential. TNT transformation was not observed at 2V cell potential. For RDX, 90% and 91% of initial RDX was transformed at 5 and 10V cell potential respectively and 87% of initial RDX was transformed at 4V applied cell potential. RDX was not transformed at cell potentials less than 3V.

The Phase 2 flow-through reactor studies utilized a column identical to those used in the Phase 1 studies except that the column was operated inside an argon atmosphere glove box and the influent concentration of TNT and RDX were near solubility. Isolation from the atmosphere was intended to limit potential contamination of gas and water samples from atmospheric nitrogen.

Results indicated that 78% of the initial TNT was transformed at 5V cell potential. Nitrite, azoxynitrotoluene, and products of MW 78, 96, 98 were identified. Complementary research at the USACE indicated that transformation of approximately 20% of the initial ^{14}C-TNT activity was mineralized to Carbon Dioxide (CO_2), approximately 10% remained sorbed to the quartz feldspar sand, and approximately 51% remained in the dissolved phase of which approximately half was unreacted TNT. The experiments were conducted under the constant current condition of 20 mA. The resultant applied (cell) potential ranged from 12-15V.

Products identified during the flow-through RDX studies indicated that MNX, DNX, and nitramide are likely intermediates. MNX and DNX were detected only at very low concentration. Nitramide has yet to be verified and quantified as a transformation product. Results from the ^{14}C-RDX mass balance studies suggest that approximately 20% of the initial ^{14}C-RDX activity is mineralized to CO_2, 50% was dissolved as non-nitroso intermediate compounds and 25% remained as dissolved (unreacted) RDX.

Based on work to date, proposed reaction mechanisms include 1) Direct electrolytic degradation of the target compound at the electrode surfaces (primarily cathodic), 2) Biotic or abiotic reaction of the target compound with electrolytically generated dissolved oxygen and or hydrogen, 3) Reaction of the target compound with free radicals formed at the electrode surfaces, and 4) Alkaline hydrolysis of the target compound at the pH conditions developed at the cathode. It appears that mechanisms 2 and 4 are not significant transformation mechanisms based on these studies.

Several DoD facilites were screened as potential locations for an e⁻barrier field demonstration for energetic compounds in groundwater. Consideration was given to Cornhusker AAP, Iowa AAP and the Pueblo Chemical Depot (PCD). Discussions with DoD personnel at the PCD were initiated based on our preliminary screening criteria. A site visit was conducted to PCD on September 8, 2003 to tour the site and discuss site conditions and possible collaboration regarding a field demonstration. Promising aspects of PCD are a shallow depth to water, favorable conditions for construction of an e⁻barrier, and the opportunity to provide a lower cost alternative to an existing energetic plume pump and treat system. Site soils were also collected for preliminary geochemical evaluation and for use in preliminary treatability studies. These studies indicated that high fractional transformation of RDX is possible using an e⁻barrier approach at PCD. Additional treatability studies will be required to design and fabricate a demonstration scale e⁻barrier for PCD.

Application of ER-1234 to a field demonstration at PCD presents the logical extension of this research to a site where high potential economic benefit may be realized. Following a successful demonstration at PCD, combined with complementary demonstrations of the technology will allow for technology acceptance and potential use at many DoD facilities.

Project Background

In recent years it has become apparent that energetic compounds (e.g. TNT, RDX, Dinitrotoluene (DNT), Octahydro 1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)) are widely present in groundwater at DoD facilities (Haines, 2003; Spain, 2000). Furthermore, it has been recognized that dissolved energetic compounds are difficult to treat using available technology. Innovative technologies that are currently being considered for management of plumes containing energetic compounds include bioremediation and zero valent iron barriers. Each of these approaches has demonstrated some success in the management of aqueous phase explosive plumes. Unfortunately, application of these technologies to energetic compounds may be constrained by effectiveness and/or cost. Of primary concern is the potential that incomplete degradation of the energetic compound will result in compounds that may pose a greater risk than the original. Reflecting on the scope and nature of the problem, there is a need for new technologies that can cost effectively address potential risks posed by energetic compounds in groundwater.

e⁻barriers - Since 1998, a primary focus of our research at CSU has been the idea that panels of permeable electrodes can be placed through groundwater plumes (transverse to flow) and operated such that target compounds are either mineralized or immobilized. The underlying principle is that low voltages can be used to drive sequential oxidation (positive electrode) and reduction (negative electrode) in-situ. Promising attributes include an ability to optimize redox conditions by adjusting voltage, removal of scale through periodic electrode reversal, and the ability to address mixtures of contaminants (including reaction intermediates) that degrade under either oxidizing or reducing conditions. Figure 1 illustrates the concept of a field scale e⁻barrier.
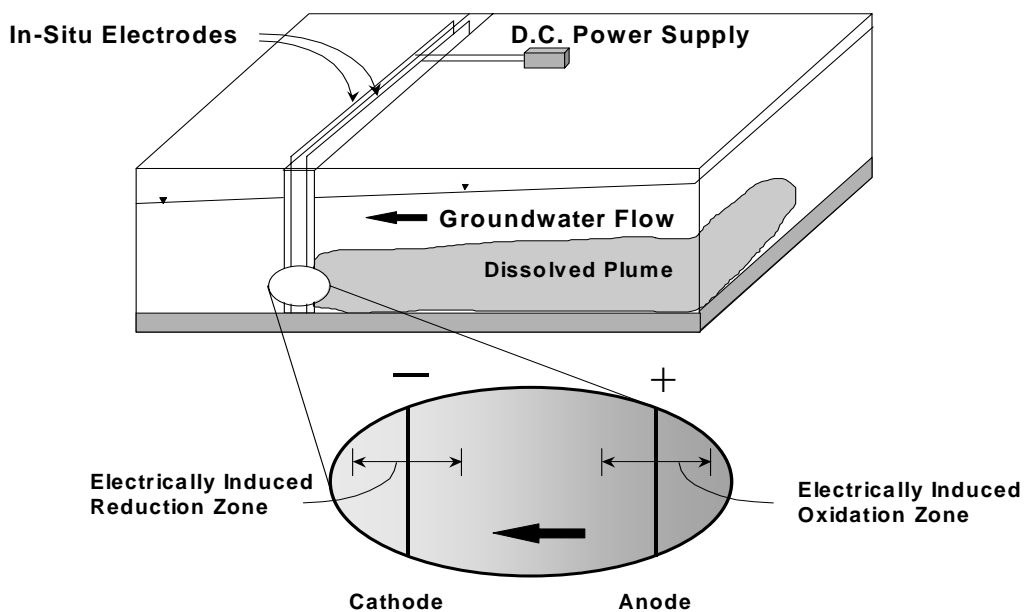
Figure 1. Conceptualization of a Field-scale e-barrier.

In 2002, SERDP funded Phase 1 proof of concept studies to evaluate the application of e⁻barrier technology to aqueous energetic compounds. Favorable findings in the Phase 1 studies led to the development of Phase 2 follow-on research conducted in 2003-04.

Project Objective

The objective of the Phase 1 research was to evaluate the efficacy of an electrically induced redox barrier to cost-effectively mineralize energetic compounds dissolved in groundwater. This objective was accomplished by conducting laboratory proof of concept experiments.

Complementary objectives of the Phase 1 research were:

- To develop fundamental scientific insights regarding electrolytic oxidation and reduction of aqueous phase energetic compounds, and
- To provide a basis for evaluating the economic feasibility of treating aqueous phase energetics via electrolytic processes.

The objective of the Phase 2 research was to further resolve reaction pathways and degradation mechanisms associated with electrolytic degradation of energetic compounds.

Complementary objectives of the Phase 2 research were to:

- Conduct mass balance studies to assist in the identification of reaction pathways, and
- Identify DoD facilities that could be used for an e⁻barrier field demonstration for energetic compounds.

Technical Approach

The Phase 1 proof of concept study consisted of two components:

1) Batch reactor voltammetry studies, intended to provide information regarding the applied voltage necessary to transform dissolved energetic compounds and,
2) Flow through column reactor studies to evaluate the applicability of the e⁻barrier for in-situ treatment of groundwater contaminated with TNT and RDX.

Primary elements of the Phase 2 research were:

1) Batch reactor studies designed to provide information regarding reaction pathways, transformation kinetics, and reaction mechanisms, and
2) Flow-through column reactor studies intended to conduct mass balance studies and to provide information regarding reaction pathways.

Details are described in the following text.

Phase 1 - Batch Reactor Voltammetry Study

Specific objectives for the first phase of the experiment include:

- Obtaining a preliminary indication of the potential to degrade energetic via electrolytic processes,
- Identifying threshold electrical potentials that drive electrolytic degradation of energetic compounds,
- Developing estimates of reaction rates,
- Gaining insight as to the relative electrolytic reactivity of TNT, RDX, HMX, and DNT,
- Verifying the use of titanium electrodes coated with mixed metal oxides for the flow through electrolytic reactor studies.

To examine the potential to electrolytically degrade aqueous energetic compounds and to understand threshold electrical potentials required, batch voltammetry experiments were conducted. The batch reactors consisted of 1L Erlenmeyer flasks fitted with matched Elgard ^{TM} expanded titanium -mixed metal oxide electrodes (Figure 2). Test solutions of TNT, RDX, HMX, and 2,4-DNT (20 µM in deionized water) were added to four separate batch reactors. In addition, a fifth control reactor (deionized water only) was operated concurrently. All reagents used in the experiments consisted of analytical grade components purchased from AccuStandard, Inc. (New Haven, Connecticut). Electrical potential was applied to the electrodes in a stepwise increasing mode using a DC power supply (GW model GPS-3030D). Resultant amperage was measured using a Fluke^{TM} 89IV multimeter. Recorded values reflect steady state conditions.
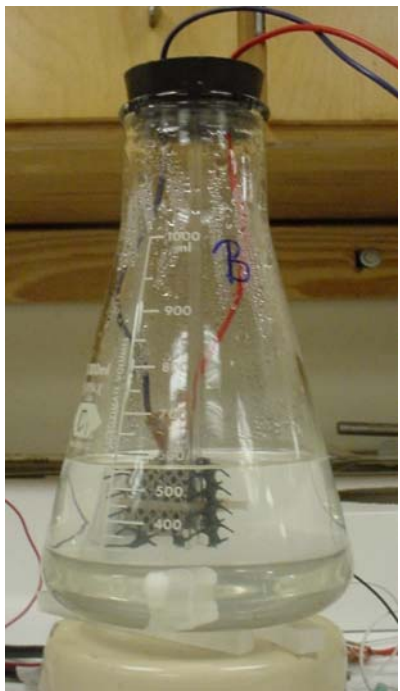
Figure 2. Batch Reactor used in the Phase 1 Voltammetry and Kinetic Experiments.

Phase 1- Flow-through Column Reactor Study

The specific objective of the Phase 1 flow-through reactor study was to evaluate the potential of an e⁻barrier approach to transformation of energetic compounds in groundwater. The envisioned field application of this research is that of an electrolytic permeable reactive barrier. Natural hydraulic gradients in groundwater drive target compounds through porous electrodes (normal to flow). At the electrodes, oxidizing and reducing conditions are sequentially imposed and target compounds are mineralized. Simulation of this process at a laboratory scale was accomplished using flow through electrolytic reactors as shown in Figure 3 and Figure 4.
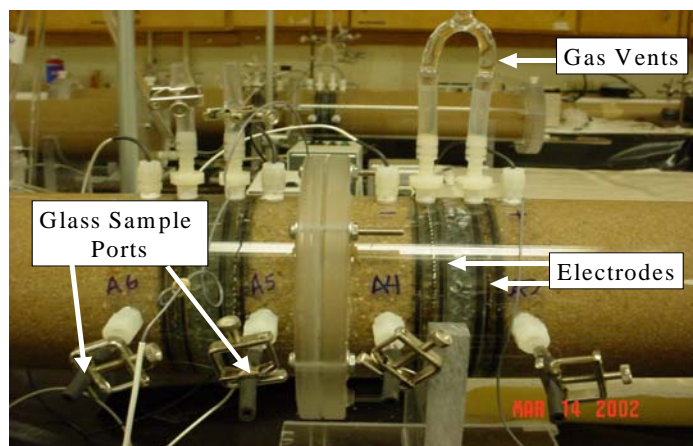
Figure 3. Detail of Electrodes in the Phase 1 Column Reactors.
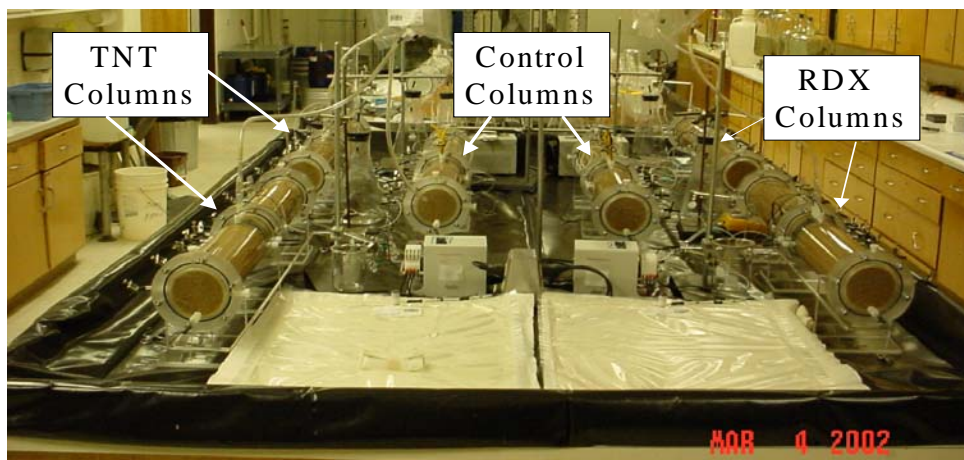
Figure 4. Setup of six Flow-Through electrolytic Reactors used in Phase 1 Experiments.

The flow-through reactors consisted of Plexiglas columns, 90 cm in length with an interior diameter of 10 cm. Two sets of titanium-mixed metal oxide electrodes were placed at the mid-point of the columns. The second set of electrodes reflects the concept that multiple sequences of oxidation and reduction could be employed. Each column was fitted with glass sample ports along the length of the column, Ag/AgCl reference

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electrodes, and gas vents. The space between and adjacent to the electrodes was packed with 6mm glass beads. The remainder of the column was packed with 16-40 quartz feldspar sand intended to approximate an aquifer matrix.

Influent RDX and TNT solutions were prepared using Fort Collins, Colorado city water (calcium-carbonate type; TDS ~70 mg/L). The water was spiked with RDX and TNT analytical grade standards purchased from AccuStandard, Inc., New Haven, CT. Influent RDX and TNT concentrations were 2.25 µM (0.5 mg/L) and 4.40 µM (1.0 mg/L), respectively. Influent solutions to the column were stored in 20 L Tedlar^{TM} bags with zero headspace and covers to limit photodegradation of the target compounds. Solutions were pumped through the columns at a rate of 0.5 mL/min using an ISMATEC^{TM} multi-channel peristaltic pump equipped with Viton^{TM} tubing. This resulted in seepage velocities of 0.3 m/day. Effluent solutions were discharged to 2 L Erlenmeyer flasks. Other than minor Viton^{TM} pump tubing sections all plumbing consisted of small diameter glass tubing. Direct current was provided using a GW^{TM} Model GPS-W3030D DC power supply.

A total of 6 identical column reactors were constructed (Figure 4). For both TNT and RDX, one column was operated in a positive-negative mode (oxidation-reduction), one column was operated in a negative-positive mode (reduction-oxidation), and one column was a zero voltage open circuit control. The control reactors provided data regarding losses of aqueous phase TNT and RDX due to adsorption to matrix materials and other processes. Comparison of results from the active column reactors to the control columns provides a basis for quantifying removal via electrolytic processes.

Over the course of the experiment, electrical potentials of 5, 10 and 15V were applied to the active reactors. Influent and effluent samples were collected at each voltage through time to quantify removal and to determine whether steady state conditions had been achieved. Samples were analyzed by GC/MS. In addition, samples were collected from glass sample ports located along the column at an applied electrical potential of 5V. These samples were analyzed by HPLC. The use of HPLC reflects greater accuracy (than the previously employed GC-MS analytical method) at low concentrations.

Other parameters measured to evaluate reactor performance were:

- Applied voltage
- Resultant amperage
- Electrode potentials
- Eh, pH, specific conductance

Phase 2 - Batch Reactor Studies

Specific objectives for the Phase 2- Batch Reactor Studies included:

- Evaluation of oxidative (anodic) and reductive (cathodic) transformation of energetic compounds at several applied (cell) potentials,
- Identification of intermediate compounds formed through anodic and/or cathodic degradation, and
- Estimation of reaction rates.

To conduct the batch reactor studies, a reaction vessel was designed to allow for optimum (2 cm) electrode spacing (Figure 5). The reactor consisted of a single reaction vessel containing separate anode and cathode chambers of approximately 1 L each. The anode and cathode were identical material consisting of expanded Ti-mmo. A Nafion™ membrane separated the electrodes. Each chamber was thoroughly mixed by magnetic stirrers. Test solutions of TNT (~500 uM) and RDX (~100 uM) were introduced into each chamber. Reagents used in the experiments consisted of research grade TNT (Chem Service, Inc. West Chester, Pennsylvania) and Grade II RDX (BAE Systems, Kingsport, Tennessee). Reagents were initially dissolved in HPLC grade methanol prior to introduction to the reaction vessel. The entire reaction vessel was covered to limit photodegradation of the energetic compounds. Voltage ranging from 2-10V cell potential was applied using a DC power supply (GW model GPS-3030D). Resultant amperage was measured using a Fluke^{TM} 89IV multimeter. Electrode potentials, Eh, pH, target compound concentrations, and formation of degradation intermediates were measured over time.
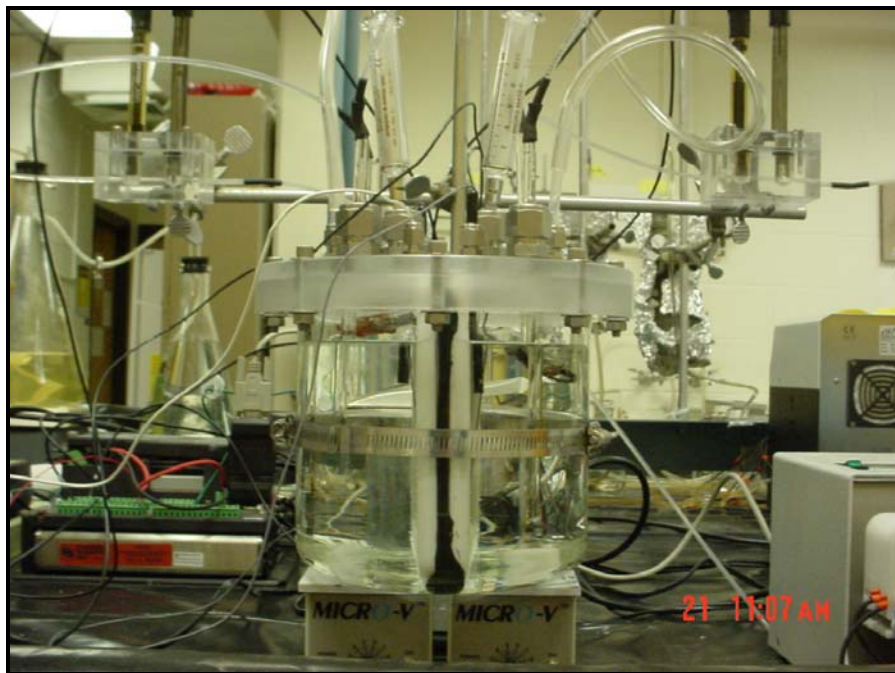
Figure 5. Phase 2 Batch Reactor.

Phase 2 - Flow-through Column Reactor Studies

Specific objectives of the Phase 2 flow-through column reactor studies were:
- To resolve electrolytic transformation pathways in a flow-through system analogous to a field scale e⁻ barrier and,
- To conduct mass balance studies based on carbon and nitrogen.

The flow-through reactor used in the study was identical to the flow-through reactors used in the Phase 1- Flow-through reactor study (Plexiglas column, 90 cm in length with an interior diameter of 10 cm, single set of Ti-mmo electrodes placed at the mid-point of the column). The column was fitted with glass sample ports along its length, Ag/AgCl reference electrodes, and gas vents. The space between and adjacent to the electrodes consisted of packed glass beads. The remainder of the column was packed with 16-40 quartz feldspar sand intended to approximate an aquifer matrix. The column and all supporting equipment is isolated from the atmosphere in an airtight enclosure (PlasLabs) to allow for quantitation of nitrogen gas that may be generated by degradation of the target compounds. The atmosphere within the glove box was maintained using argon gas and monitored for infiltration of ambient air (BW Technologies).

Influent RDX and TNT solutions were prepared using Fort Collins, Colorado city water (calcium-carbonate type; TDS ~70 mg/L). The water was spiked with RDX and TNT at 100 uM and 500 uM respectively. Influent solutions to the column were stored in 20L Tedlar^{TM} bags with zero headspace and covers to limit photodegradation of the target compound. Test solutions were pumped through the column reactors at a rate of 0.5 mL/min using an ISMATEC^{TM} multi-channel peristaltic pump equipped with Viton^{TM} tubing.

The resultant seepage velocity was approximately 0.3 m/day. Effluent solutions were discharged to 2L Erlenmeyer flasks. Other than minor Viton^{TM} pump tubing sections all plumbing consisted of small diameter glass tubing. Direct current was supplied to the electrodes using a GW^{TM} Model GPS-W3030D DC power supply.

For the mass balance studies, an electrical potential of 5V was applied to electrodes. Influent and effluent samples were collected over time to conduct the mass balance. Additionally, samples were collected from the sample ports along the column to evaluate spatial changes in target compound and reaction product distribution. Samples were analyzed by LC/MS for explosive and intermediate compounds. Volatile products were identified by GC/MS. Nitrate and nitrite were measured using ion chromatography.

Other parameters measured included:

- Applied voltage
- Resultant amperage
- Electrode potentials

Radiolabeled Mass Balance Studies

Because of the difficulty associated with achieving mass balances conducted in the argon atmosphere glove box, a radiolabeled study quantifying the products of electrolytic transformation using ^{14}C-TNT and ^{14}C-RDX was conducted. The experiments were conducted in two steps: initial reactor testing using ^{12}C-TNT and ^{12}C RDX followed by the mass balance experiments using ^{14}C-TNT and ^{14}C RDX. These experiments were conducted in cooperation with the USACE ERDC located in Vicksburg, Mississippi. The materials, analytical equipment and methods differed from those used at CSU and are discussed below.
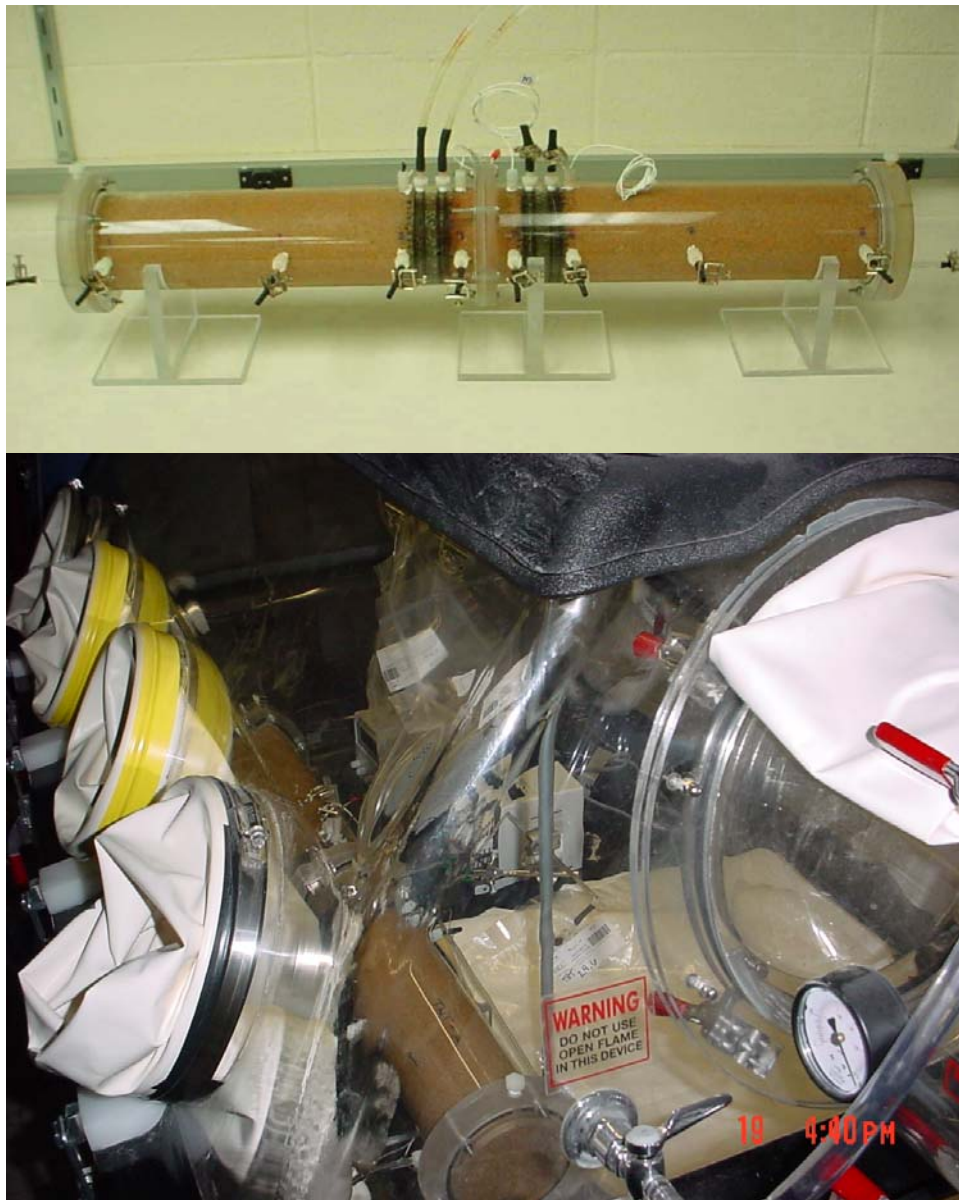
Figure 6. Column Reactor (top) and Glove Box (bottom) used for Phase 2 Flow-Through Column Studies.

Analytical Methods (Colorado State University)

Sample Preparation

All samples were collected in glass vials and stored at $4^{\circ}C$ prior to analysis. Samples collected during the Phase 1 research were preconcentrated using Waters Porapak RDX cartridges according to manufacturer specifications. Samples collected during the Phase 2 research did not require preconcentration prior to analysis.

HPLC

Analysis for energetic compounds was conducted using HPLC (Hewlett-Packard Series 1100) equipped with a Waters XTerra RP C_{18} column (2.1 x 50 mm) or a Waters Phenyl column. Compounds were quantified by UV at 230 nm or 254 nm.

LC/MS

Mass spectrometric analysis for verification of energetic compounds and for identification of unknown compounds were conducted using the above described HPLC followed by a Finnegan LCQ Duo Mass Spectrometer. Introduction to the mass spectrometer was conducted using electrospray ionization in the negative mode. Capillary potential used was 4.5 kV at a temperature of 140C.

GC/MS

Energetic compounds and volatile intermediates were determined using GC/MS (Agilent Series 6890 and Agilent 5973 Mass Selective Detector).

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Nitrate and nitrite were determined using ion chromatography (Dionex DX 120, IonPak AS14 column).

Eh-pH

pH measurements were made with a combination pH/reference electrode (Ag/AgCl). Eh (pe) measurements were made with a combination platinum/reference (Ag/AgCl) electrode. Electrodes were connected to a Campbell Scientific CR10X datalogger or Denver Instruments AP25. Eh measurements were corrected to reference the standard hydrogen electrode. Conversion to pe was made using the relationship:

$$pe = \frac{Eh}{2.3RTF}$$

where: R= gas constant

       T= absolute temperature

       F= Faraday constant (96,490 C mol^{-1} at 25°C)

Materials and analytical equipment used for the radiolabeled 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitiro-1,3,5-triazine (RDX) mass balance studies United States Army Corps of Engineers (USACE) Engineer Research and Development Center (ERDC)

Study Materials

RDX and TNT used in the ^{12}C-RDX and ^{12}C-TNT phase of the experiments were obtained from ERDC laboratory stock. Radiolabeled RDX and TNT were obtained from Perkin Elmer Life Sciences (Shelton, CT). RDX and TNT calibration standards for EPA Method 8330 were obtained from Supelco (Boston, Massachusetts).

Test solutions were prepared by dissolving either RDX or TNT in a calcium carbonate type water (300 uS cm^{-1}). Test solutions were intended to approximate typical groundwater concentrations observed at ammunition manufacturing sites (RDX 2.5 uM; TNT 5.0 uM).

Plexiglas columns identical to those used in the Phase 1 experiments described above were used as one-dimensional analogs to an in-situ application of an electrolytic reactive barrier. The experimental setup consisted of a horizontally mounted column (96 cm x 10 cm ID) containing a single set of electrodes. The electrode materials consisted of the same expanded Ti-mmo used in previous experiments mounted at 38 (anode) and 40 cm (cathode) from the inlet to the column. The treatment sequence was sequential oxidation and reduction. The interelectrode space consisted of 6 mm glass beads to maintain electrode spacing at 2 cm. The remainder of the column was packed with quartz-feldspar sand intended to approximate aquifer material. The columns were fitted with Ag/AgCl reference cells installed in the immediate vicinity of the electrodes to measure electrode potentials. Eight glass sample ports spaced along the length of the column allowed for collection of aqueous samples for analysis. Test solutions (RDX or TNT) were pumped through the column using a Masterflex peristaltic pump at a flow rate of 0.6 mL min^{-1} (approximate seepage velocity of 0.3 m day^{-1}). The columns were operated in a constant current mode (20 mA) for the TNT study and a stepped current mode (10 mA and 20 mA) for the RDX study. This mode of operation resulted in an applied (cell) potential range of 5-15V.

The primary analysis was to measure RDX and TNT concentration influent to the column, effluent from the column in the aqueous phase and measurement of gaseous losses resulting from electrolytic mineralization. Secondary analysis involved measurement of RDX and TNT concentration as a function of position in the column.

HPLC Analysis

The analysis of RDX, its nitroso-substituted transformation products, TNT and its daughter products was performed using a DIONEX HPLC system comprising of a P580 fluid pump, ASI-100 autosampler, and UVD340U absorbance detector. Separation was achieved using a Supelco CN reverse-phase HPLC column (25 cm by 4.6 mm) with a Novapak C-18 precolumn for the primary column. The mobile phase comprised of 1:1 (volume per volume) methanol/organic-free reagent water at a flow rate of 1 mL/min. Explosives absorbance was monitored at 245 nm.

IC

Nitrate and nitrite were analyzed on a DIONEX Ion Chromatograph. Separation and detection were achieved using an Ionpac AS11 analytical column and a Dionex conductivity detector. The mobile phase consisted of NaOH at a flow rate of 1.5 mL/min.

Liquid Scintillation Counting (LSC)

Sample radioactive concentration via liquid scintillation counting was conducted on 2500 TR Packard Scintillation Counter (Packard Biosciences). The counter was equipped with a barium external source to enable correction for machine efficiency. The liquid scintillation protocol collected data up to 156 meqV, which is the maximum energy for $[^{14}C]$. Each sample was counted twice for two minutes.

Eh-pH

Oxidation-reduction potential (ORP) and pH were measured with Oakton WD-35100-00 model pH/ORP Controllers (Cole-Parmer, Vernon Hills, Illinois) with a measuring range of 0 to 14 for pH and -1250 to 1250 mV ORP. ORP was measured using a Cole-Parmer combination redox electrode with platinum sensing surface and Ag/AgCl reference electrode. The value Eh was obtained by adding the standard potential of the reference electrode (202 mV at 25°C) to the measured potential. pH was determined with a Cole-Parmer combination electrode.

Results and Accomplishments

Phase 1 - Batch Reactor Voltammetry Study

The batch reactor voltammetry study was conducted over an imposed (cell) potential range of 0-20V (Figure 7). Observations drawn from the data include:

1. Deviations in resultant amperage from the control reactor (~7.5V) suggests the target compounds can be degraded via electrolytic processes, and
2. That the relative electrolytic reactivity the tested compounds is 2,4-DNT>HMX> TNT>RDX.
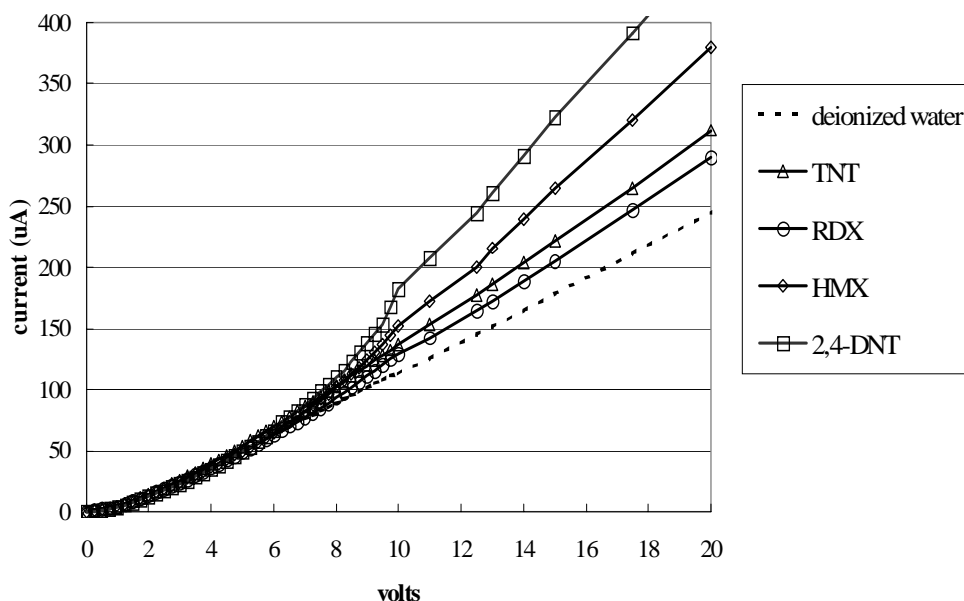
Figure 7. Voltammetry Results from Batch Reactor Experiments.

Estimation of Reaction Rates - Using the same batch reactors, a second experiment was conducted to estimate the half-life of TNT and RDX. Twenty μM solutions were prepared using deionized water and exposed to an electrical potential of 12.5V for 300 minutes. Resultant amperage was recorded and aqueous samples were collected at 0, 10, 30, 60, 120, and 300 minutes. Samples were preconcentrated by solid phase extraction (Waters Porapak RDX cartridges). Extractants were analyzed for target compounds and degradation products using GC-MS.

Concentration versus time data is presented in Figure 8. The half-life for TNT and RDX were 430 and 990 minutes, respectively. No significant intermediate compounds were observed. Consistent with the findings of the voltammetry experiment, TNT is degraded more rapidly than RDX. It is important to note that the rates reflect the configuration of the reactor as much as the reactivity of the compounds.   As such, it is difficult to transfer the measured half lives to other systems.
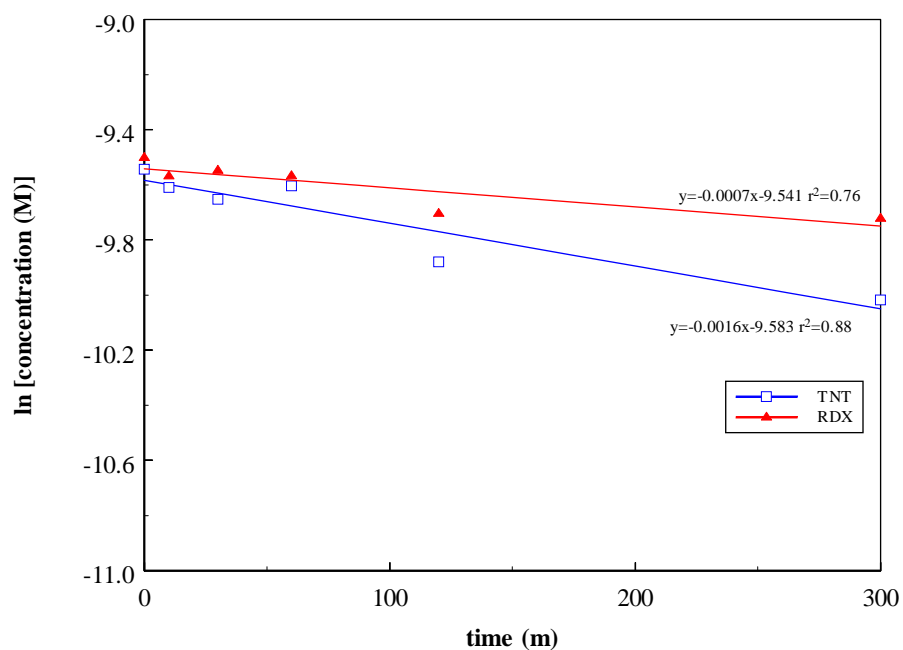
Figure 8. Concentration of TNT and RDX as a Function of Time in Batch Reactors Operated at 12.5 volts.

Testing of Alternate Cathode Materials – Finally, the batch reactors were used to test different cathode materials. Titanium, copper, and stainless steel cathodes were matched with titanium-mixed metal oxide anodes in separate flasks. Twenty µM solutions of TNT were placed in each reactor. Aqueous samples were collected over the period described above and analyzed for TNT. Estimated half-life values suggest that improved performance is not likely using uncoated titanium, copper, or stainless steel as the cathode material (Table 1).

Table 1. Calculated TNT Half-life as a Function of Batch Reactor Cathode Materials.

Cathode material	TNT half-life (minutes)
Titanium-mixed metal oxide	430
Titanium	1700
Copper	>2000
Stainless steel	>2000

In summary, the batch experiment provided a relatively simple basis for evaluating the potential to treat TNT, RDX, HMX, and DNT via electrolytic processes. All compounds appear to be degradable via electrolytic processes with the order of reactivity being 2,4-DNT>HMX> TNT>RDX. Furthermore, the batch test provided a basis for using titanium mixed metal oxide for both the anode and the cathode in the flow through electrolytic reactor experiments described in the following text.

Phase 1 - Flow-Through Reactor Experiments

Effluent Comparison - The primary focus of the Phase 1 experiment was to evaluate whether aqueous energetic compounds (as represented by TNT and RDX) could be degraded in a flow through electrolytic reactor. Initially, transformation fractions relative to the control reactors for TNT and RDX at the three test voltages were calculated based on GC/MS analysis (Table 2-Table 3). Under sequential oxidation-reduction (positive-negative sequence), high fractional transformation of both TNT and RDX was observed. Additionally, sequential reduction-oxidation (negative-positive sequence) resulted in lower fractional transformation for both test compounds. The high transformation rate observed at 5V in the TNT reactor (negative-positive sequence) may be due to more favorable Eh conditions downstream of the electrodes.

Calculated transformation fraction under sequential oxidation-reduction (positive – negative sequence) is based on effluent concentration in the test columns relative to the control columns (Figure 9, Figure 10). In all cases the effluent concentrations from the test columns were below the practical quantitation limits (PQLs). The values included in Figure 9 and Figure 10 for the test reactors are the PQLs and provided the basis of the estimated transformation. Actual effluent concentrations from the test reactors (sequential oxidation and reduction) were below the PQLs. As such, positive-negative sequence results in Table 2 and Table 3 are qualified as greater than. Variability of the reported positive-negative sequence results (PQLs) reflects varying sample volume (solid phase extraction procedure).   The mean GC/MS PQLs for the experiment were 10 ug/L for TNT and 40 ug/L for RDX. More rigorous insight into transformation rates is presented in the following text describing concentration as a function of position in the reactor.

Table 2. TNT Removal Based on GC/MS Analysis Relative to Control at the Three Test Voltages.

Applied Voltage	Percent TNT removed relative to control reactor	
	Positive - negative sequence	Negative – positive sequence
15	>97 %	37 %
10	>97 %	45 %
5	>98 %	89 %

Table 3. RDX Removal Based on GC/MS Analysis Relative to Control at the Three Test Voltages.

Applied Voltage	Percent RDX removed relative to control reactor	
	Positive - negative sequence	Negative – positive sequence
15	>90 %	29 %
10	>90 %	43 %
5	>90 %	49 %
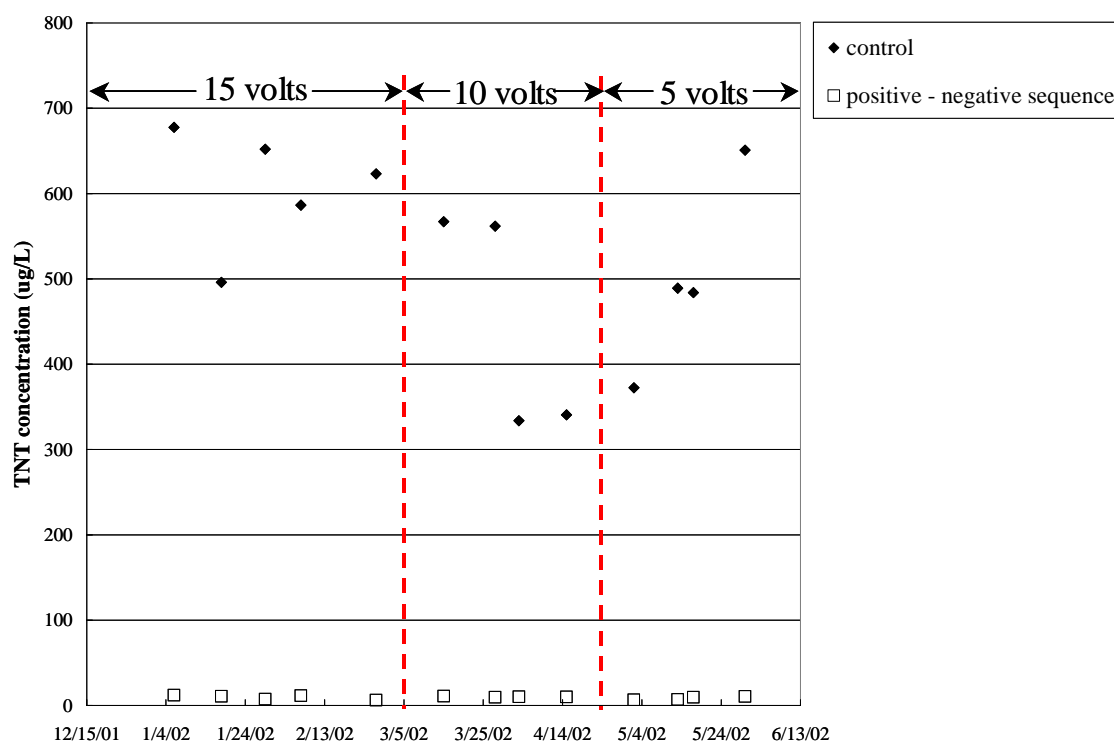
Figure 9. TNT Effluent Concentrations (GC/MS) from the Control Reactor and Positive – negative electrode sequence.
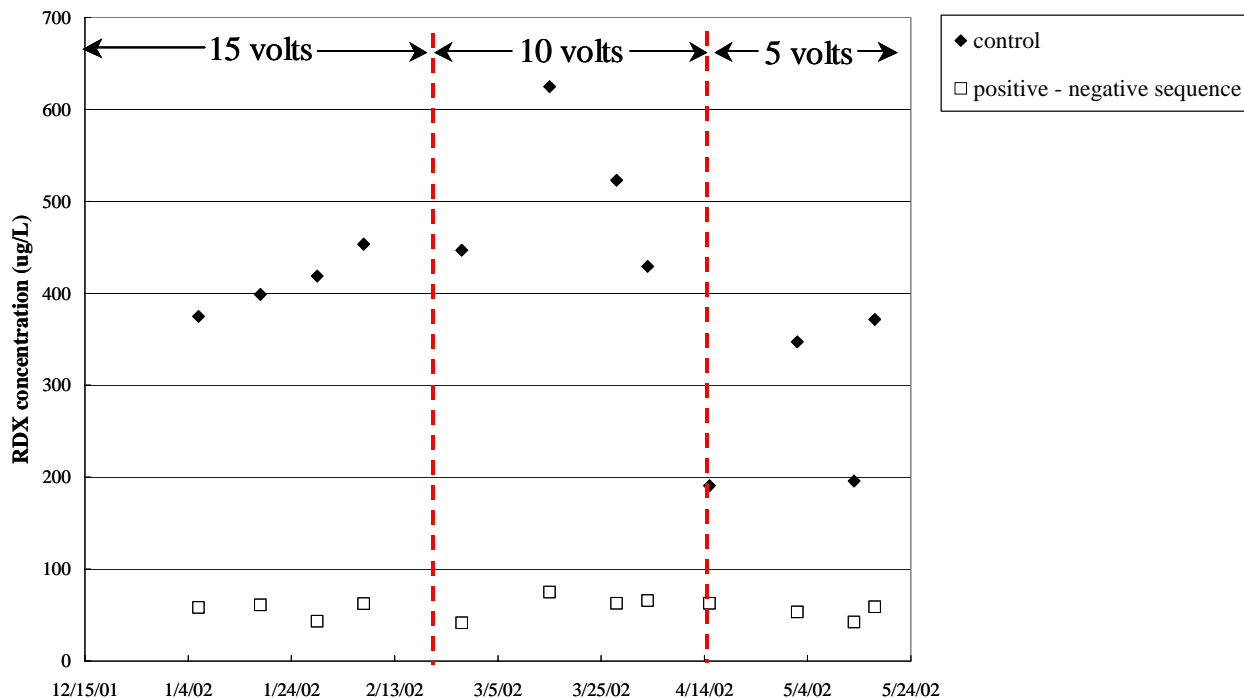
Figure 10. RDX Effluent Concentrations (GC/MS) from the Control Reactor and Positive - negative electrode sequence.

Concentration as a Function of Position - Concentration profiles were developed for an applied potential of 5V (Figure 11 and Figure 12.) It can be seen that for both target compounds, degradation relative to the control column occurred upstream and downstream of the electrodes (position 0). Losses of target compound because of adsorption or other processes are also illustrated in Figure 11 and Figure 12 (control columns). Estimated practical quantitation limits for TNT and RDX using HPLC-UV are 5 and 10 ug/L respectively. Transformation rates in the positive-negative sequence (sequential oxidation reduction) test reactors calculated using HPLC generated concentrations were 97.6% for TNT and 98.1% for RDX relative to the control reactors. This result correlates well with the TNT values reported above, but suggests that the RDX transformation rates reported based on GC/MS analyses may be low. This result also illustrates the lower quantitation limit relative to the GC/MS method.

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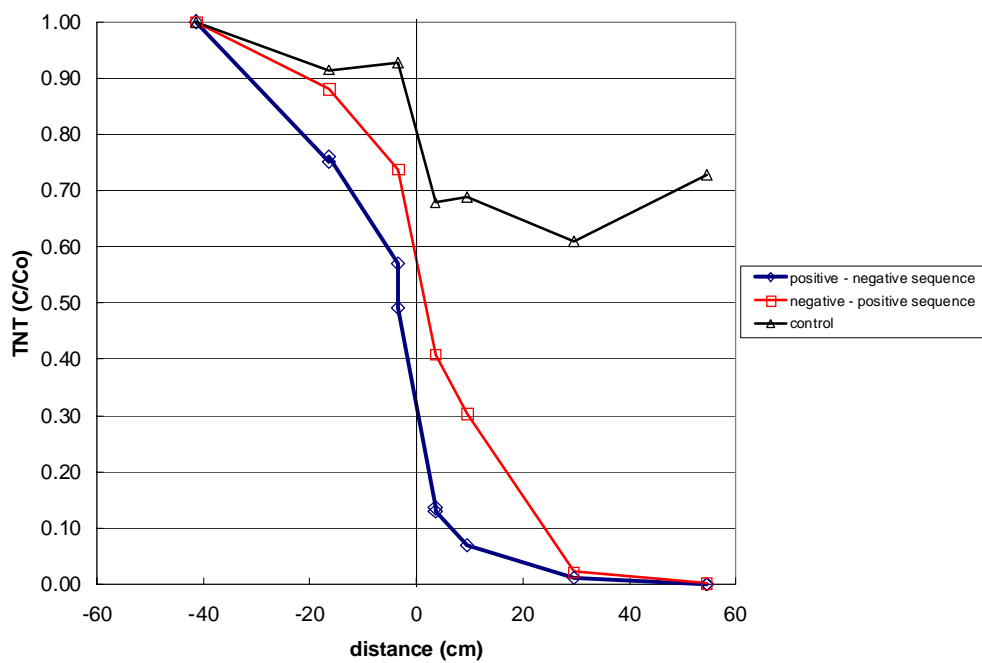
Figure 11. Normalized TNT Concentration Profile at 5V.

**Flow
Direction**
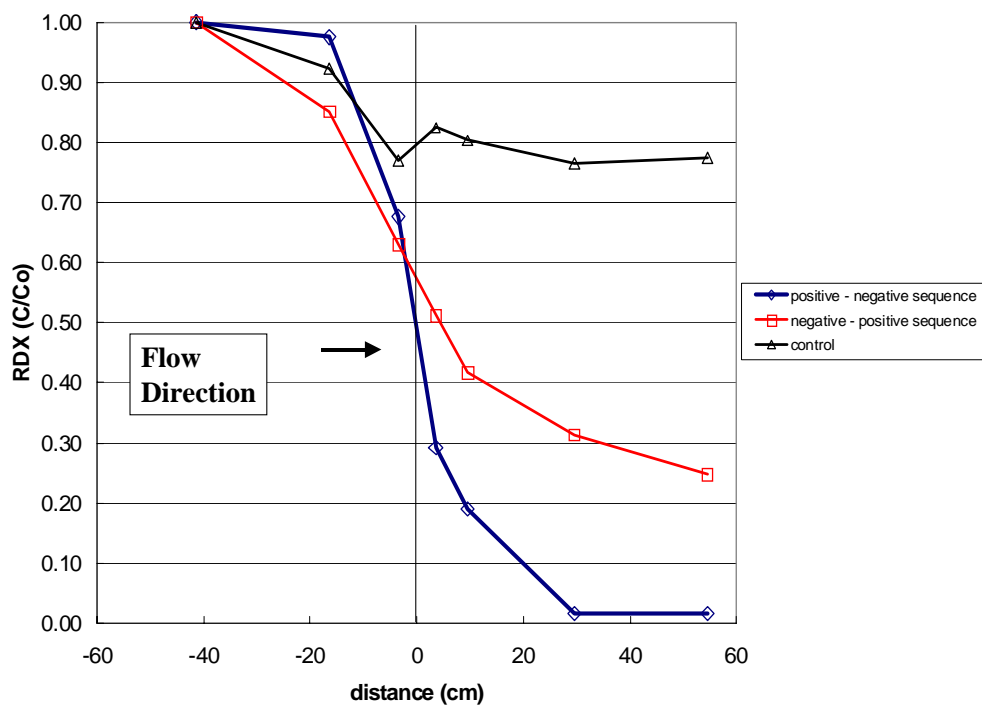
Figure 12. Normalized RDX Concentration Profile at 5V.

Shifts in pH and pe - Central to the e⁻barrier approach is the ability to affect changes in pH and pe electrically. pH shifts were measured as a function of position in the columns at the three test voltages (Figure 13.) It can be seen that under sequential oxidation-reduction that pH remains constant at all test voltages. Under sequential reduction – oxidation however, pH shifts were more significant. This result suggests that degradation processes are not substantially influenced by shifts in pH, since the highest removal rates were observed under sequential oxidation-reduction. Work by others indicates that pH above 10 is required to observe significant alkaline hydrolysis of nitroaromatics and nitramines (Davis, 2002), our results suggest that alkaline hydrolysis may not contribute significantly to the overall degradation observed. This does not preclude alkaline hydrolysis as a significant degradation mechanism in other systems, however.

Substantial shifts in Eh were measured in the reactors under both electrode sequences (Figure 14). This result suggests that pe (or combined pe and pH) shifts may be necessary for the observed degradation. Another significant finding was increased removal under sequential reduction-oxidation at 5V relative to 10 and 15V. This may be the result of lower Eh achieved under 5V (Figure 14.) This behavior is under investigation.
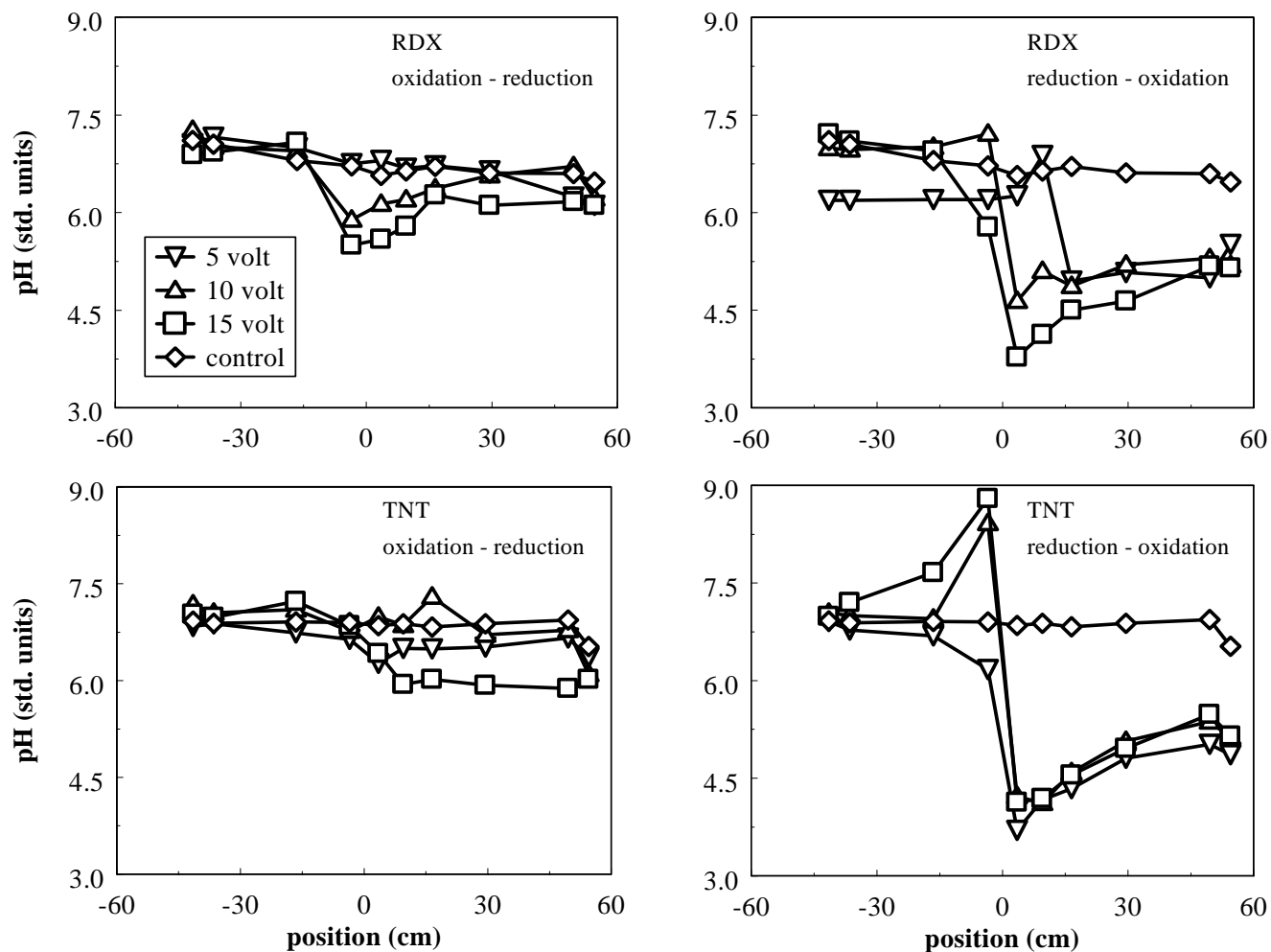
Figure 13. pH Measurements as a Function of Position in the Reactors. Position 0 = location of the electrodes.
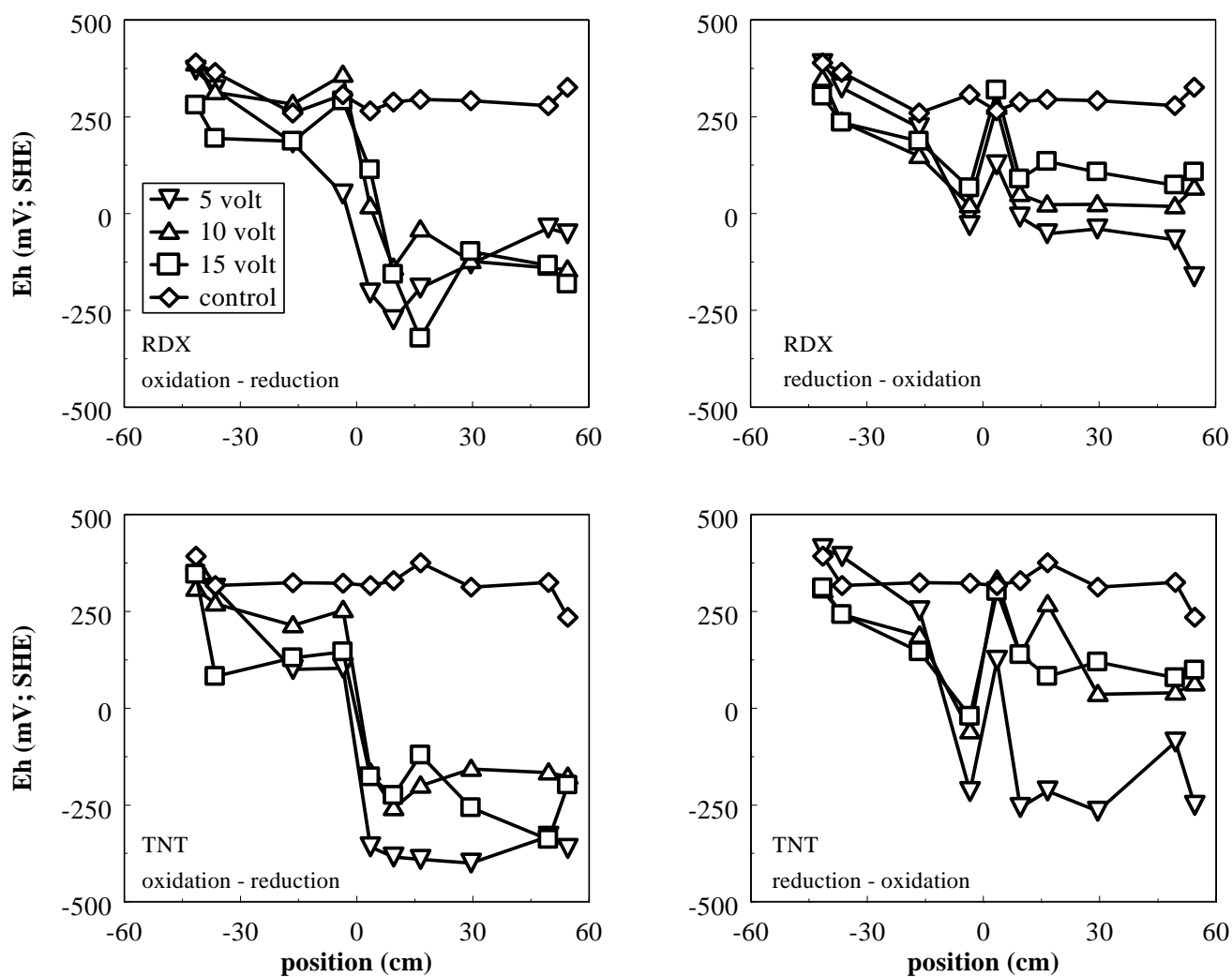
Figure 14. Eh Measurements as a Function of Position in the Reactors. Position 0 = location of the electrodes.

Intermediate Compound Identification – For the Phase 1 experiments (proof of concept level), only those degradation intermediate compounds that were commercially available were evaluated. The following TNT degradation intermediates were explicitly included in the search:

- 2,6-DNT
- 2,4-DNT
- 1,3,5-TNB
- 1,3-DNB
- 2-NT
- 3-NT
- 4-NT
- NB
- 2-ADNT
- 4-ADNT

Additionally, volatile compounds were analyzed by GC-MS and identified by library search.

As an example, Figure 15 presents HPLC chromatograms from the TNT reactors at 15V. From the chromatograms:

- Only minor peaks (other than TNT) are observed in the reactor testing sequential oxidation – reduction, suggesting that degradation intermediates are present at very low concentration,
- Several of the minor peaks are also present in the control reactor chromatogram, suggesting that these compounds are not related to electrochemical processes,
- Minor peak observed in reactor testing sequential reduction – oxidation at 17.45 minutes is 2-aminodinitrotoluene (ADNT).

It is important to note that each sample associated with the chromatograms in Figure 15 consisted of a different extraction volume.

Of the compounds that were included in the explicit search, only 2-ADNT was identified in quantifiable concentrations and was observed only under sequential reduction-oxidation (Figure 16). Maximum 2-ADNT concentration observed was approximately 63 ug/L.
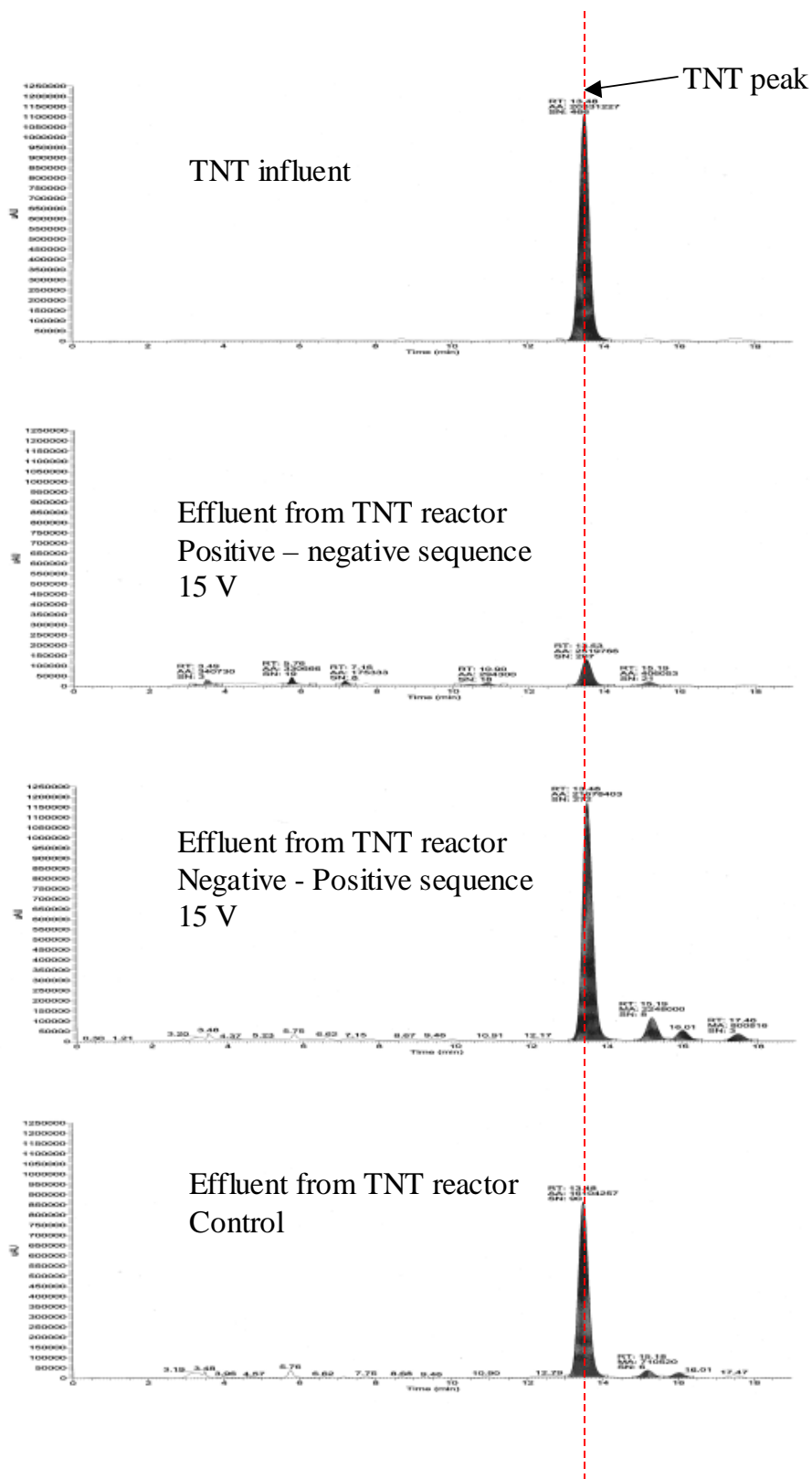
Figure 15. HPLC Chromatograms from the TNT Reactors. Top: Influent Solution; 2nd: Effluent from +- reactor; 3rd: Effluent from -+ reactor; Bottom: Effluent from Control Reactor.

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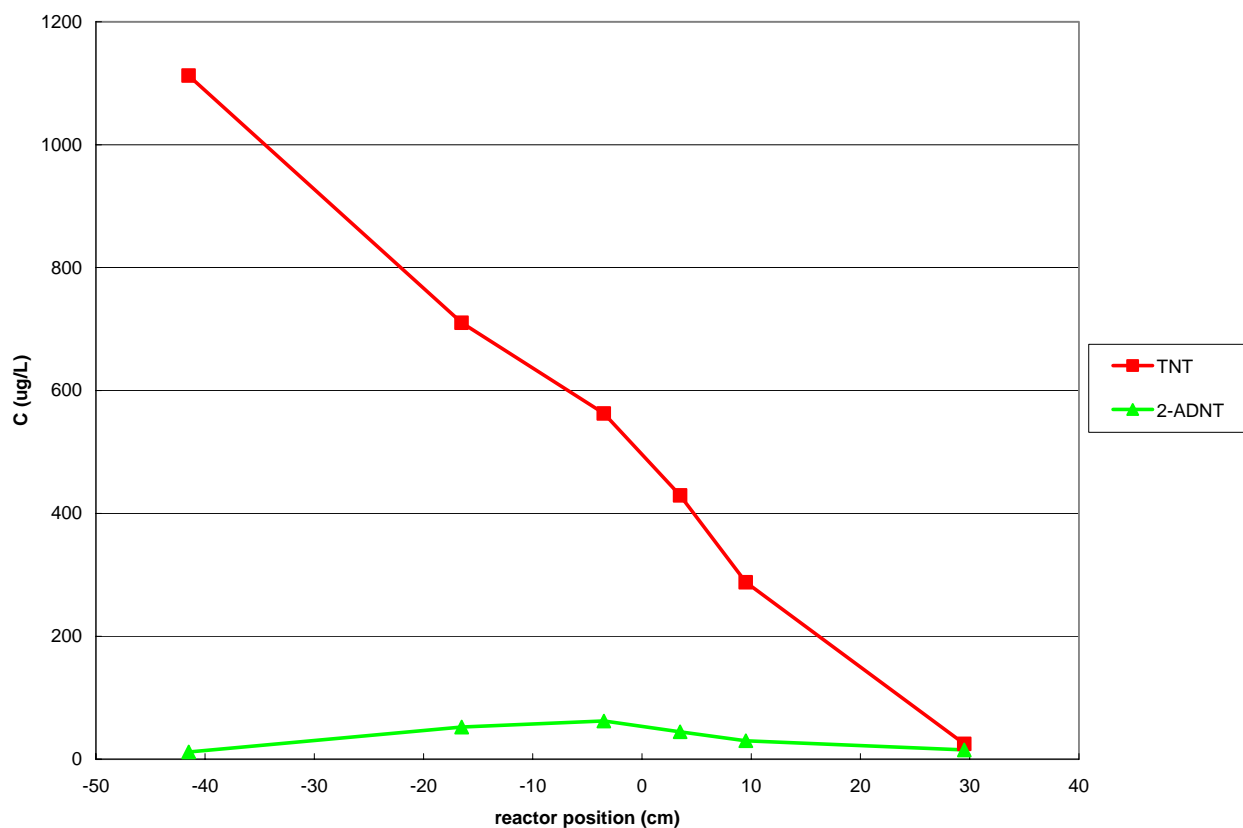
Figure 16. TNT and 2-ADNT Concentrations as a Function of Position in the Reactor Testing Sequential Reduction-oxidation.

Standard solutions for the degradation intermediates of RDX were not obtained during this phase of the research. HPLC chromatograms however, suggest that few intermediate compounds were generated under sequential oxidation-reduction (Figure 17).
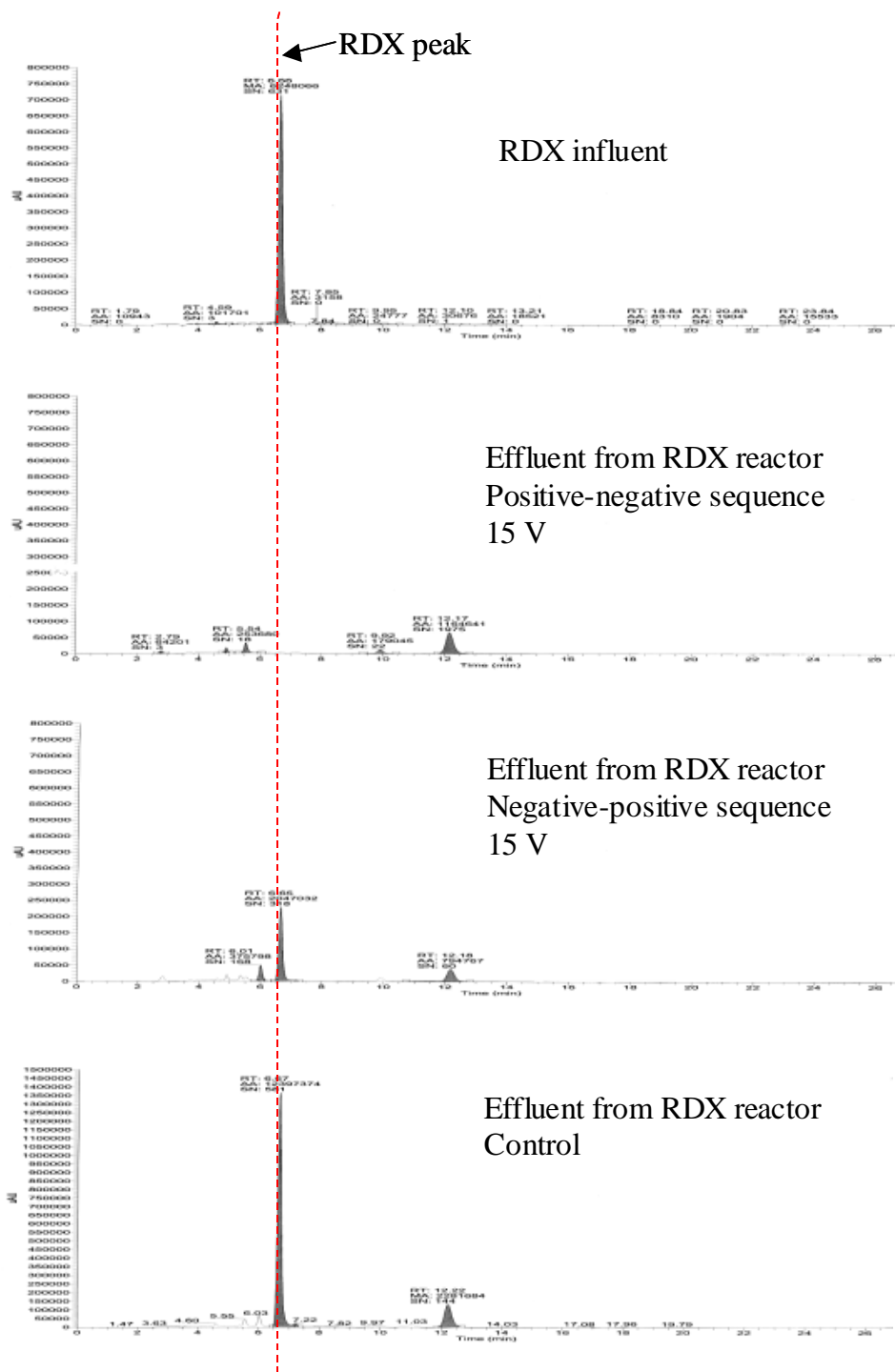
Figure 17. HPLC Chromatograms from the RDX reactors. Top: Influent Solution; 2nd: Effluent from +- reactor; 3rd: Effluent from -+ reactor; Bottom: Effluent from Control Reactor.

Power Requirement - Amperage data collected from the reactors during the experiment were used to calculate power requirements for a field scale application. These calculations are included in Table 4.

Table 4. Power requirements for test reactors used in the experiment.

Target compound (electrode sequence)	15V (W/m^2) ($/day/m^2)	10V (W/m^2) ($/day/m^2)	5V (W/m^2) ($/day/m^2)
TNT (positive-negative)	35 (0.042)*	12 (0.014)*	3 (0.0036)*
TNT (negative - positive)	38 (0.046)*	15 (0.018)*	2 (0.0024)*
RDX (positive-negative)	35 (0.042)*	14 (0.017)*	2 (0.0024)*
TNT (negative - positive)	36 (0.043)*	9 (0.011)*	1 (0.0012)*

* Assumes a power cost of $0.05/KW-hour

In summary, the Phase 1 flow-through experiments provided evidence that an electrolytic reactive barrier has the potential to treat groundwater contaminated with TNT or RDX with minimal formation of detrimental intermediate compounds for low cost. These results provided the basis for follow-on research (Phase 2) to develop insight into reaction pathways and to develop a better understanding of transformation products.

Phase 2 - Batch Reactor Studies

TNT Transformation - Measurement of TNT concentrations over time suggests that TNT was readily transformed in the cathode chamber at cell voltages above an applied potential of 2V (Figure 18).   TNT was not significantly transformed in the cathode chamber during the 2V test. Measurement of cathode potentials during the experiments (Figure 20) suggest that TNT degradation initiates at approximately –350 mV SHE as evidenced by the lag in TNT degradation during the early parts of the experiments. Reaction intermediates identified in the catholyte include DNT, compounds of MW 138 (likely aminotoluenes), 98, 96, and 78. Additional work is required to identify and quantify these compounds.

Minor TNT transformation was observed in the anode chamber at 5V and 10V cell potentials (Figure 19).   Measurement of anode potentials during the experiments (Figure 20) suggests that potentials exceeding +1100 mV SHE are required for TNT transformation at an anode. Transformation products are likely 2,4-DNT (detected by MS, but below detection by HPLC). The results also suggest that anodic oxidation of TNT is a kinetically slower process than cathodic reduction. Additional research regarding the complementary relationship between anodic and cathodic transformation is required.

Eh (pe) and pH measurements taken during the batch experiments reflect the electrolysis of water and protonation of products associated with the degradation of TNT. The observed shifts in pe and pH provide insight into the potential for homogeneous (aqueous phase) transformation by alkaline hydrolysis or homogeneous reduction. Homogeneous mechanisms do not appear significant at cell voltages below 5V, since the pH and pe conditions at 5V are not significantly different than those at 2V cell potential (during which no transformation was observed). This result suggests that the transformation reactions are primarily heterogeneous cathodic reduction reactions. Complementary experiments funded through cooperation with the USACE ERDC indicated that alkaline hydrolysis pathways of transformation of TNT and RDX are not significant in the electrolytic transformation of these compounds.

Nitrite and nitrate were formed rapidly in the cathode chamber at cell potentials above 2V (Figure 22). Nitrite was formed in higher concentration than nitrate, consistent with the reducing conditions of the catholyte.   Nitrite concentrations reached a maximum at approximately 50 minutes, 100 minutes, and 200 minutes during the 10, 5 and 4V experiments respectively. This result suggests that nitrate is further reduced to either NH_3 or $NO_{x(g)}$. At maximum concentration, nitrate and nitrite accounted for 15% of the total N in the cathode chamber.
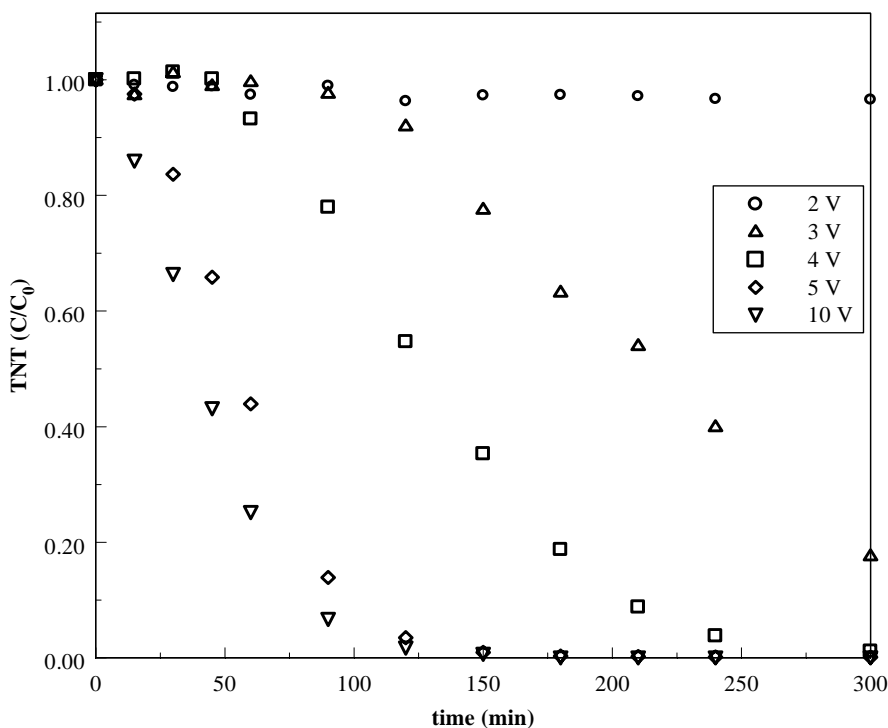
Figure 18. Normalized TNT Concentrations Measured in the Cathode Chamber.

40
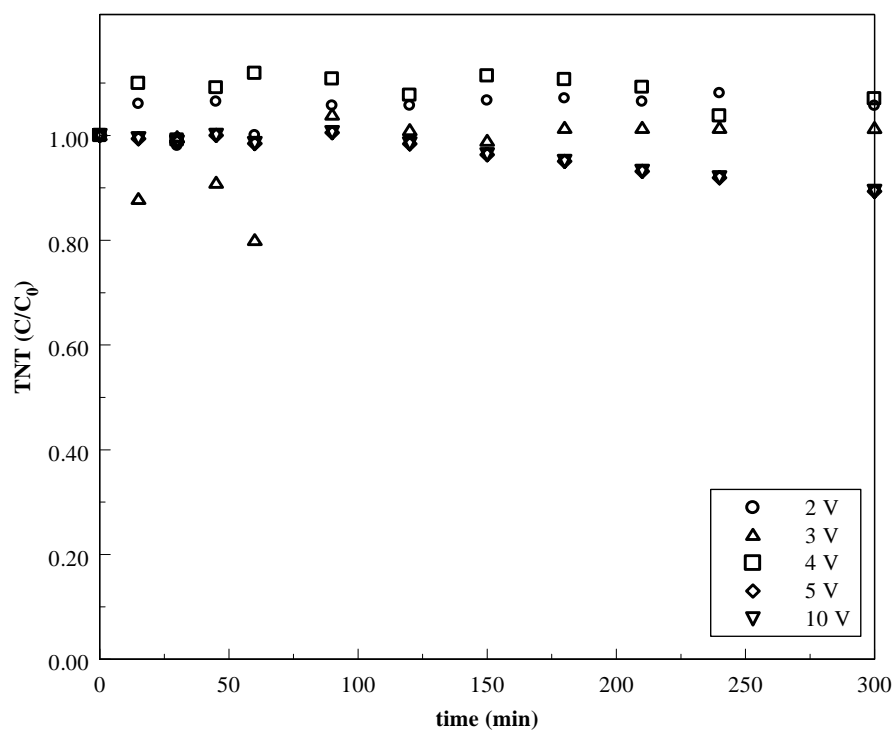
Figure 19. Normalized TNT Concentrations Measured in the Anode Chamber.

Figure 20. Cathode (left) and Anode (right) Potentials (SHE) Measured during the Phase 2 TNT Batch Experiments.
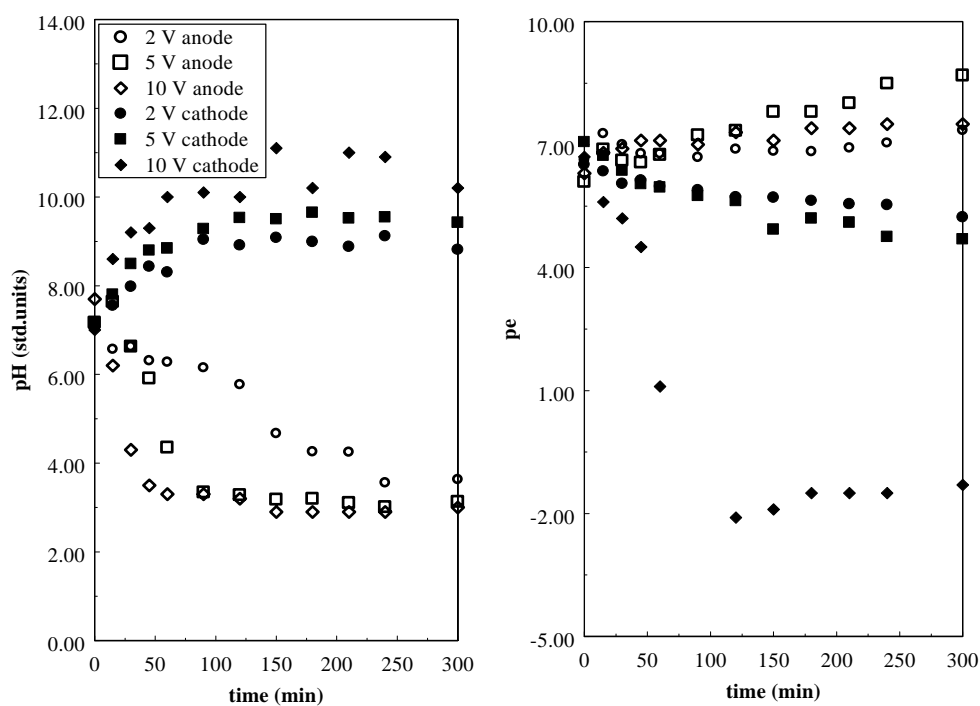
Figure 21. pH (left) and pe (right) Measurements taken during the Phase 2 Batch Experiments.
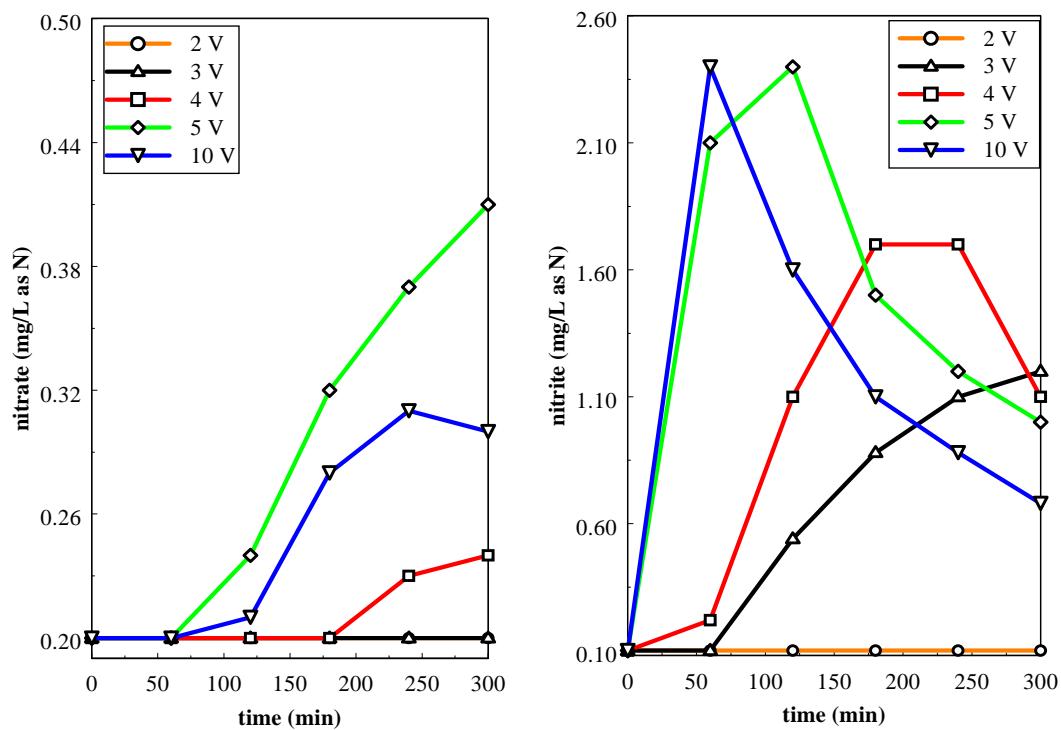
Figure 22. Nitrate (left) and Nitrite (right) Concentrations Measured in the Cathode Chamber during the Phase 2 TNT Batch Experiments.

Reaction Rates for Cathodic TNT Transformation - An estimate of reaction rates was determined based on pseudo-first order models fit to the data collected from the cathode chamber of the batch reactor (Table 5). Models are based on data collected following development of cathode potentials of <-350 mV SHE. Converting the homogeneous rate constants to heterogeneous (interphase) constants based on the cell volume and area of the electrode surface yields reaction rates that reflect dependence on surface area of electrode.

Table 5. Reaction Rate Constants for Cathodic Reduction of TNT.

Cell Voltage (V)	Rate constant (min^{-1})	Half-life (min)	Heterogeneous Rate constant (cm·min^{-1})
2	0.0001	6900	0.0007
3	0.008	87	0.0056
4	0.021	33	0.14
5	0.023	26	0.16
10	0.040	17	0.28

RDX Transformation - In contrast to TNT transformation, RDX was transformed in the cathode chamber only at cell voltages above 4V (Figure 23). RDX was not significantly transformed in the cathode chamber during the 2V and 3V experiments. Measurement of cathode potentials during the experiments (Figure 24) suggest that RDX degradation initiates at approximately –800 mV SHE as evidenced by the lag in RDX degradation during the early parts of the experiments. Reaction intermediates identified in the catholyte include MNX and nitramide indicating that reduction pathways suggested by others are likely (Bonin, et al., 2004).

As in the TNT experiments, only minor RDX transformation was observed in the anode chamber at 5V and 10V cell potentials (Figure 24). Measurement of anode potentials during the experiments (Figure 24) suggests that potentials exceeding +1500 mV SHE are required for RDX transformation at an anode. As with TNT, The results suggest that anodic oxidation of RDX is a kinetically slower process than cathodic reduction.

Eh (pe) and pH measurements taken during the batch experiments reflect the electrolysis of water and protonation of products associated with the degradation of RDX (Figure 26). The observed shifts in pe and pH provide insight into the potential for homogeneous transformation by alkaline hydrolysis or homogeneous reduction. Similar to the TNT experiments, homogeneous mechanisms do not appear significant at cell voltages below 5V, since the pH and pe conditions at 5V are not significantly different than those at 2V and 3V cell potential (during which no transformation was observed). This result suggests that the transformation reactions are primarily heterogeneous cathodic reduction reactions. This result is consistent with the findings for TNT transformation at the cathode surface.

Nitrite was formed rapidly in the cathode chamber at cell potentials above 3V (Figure 27). Nitrite concentrations reached a maximum at approximately 120 minutes, 240 minutes, and 300 minutes during the 10, 5 and 4V experiments respectively. The measured decrease in nitrite concentration observed during the 10V experiment suggests that nitrite is further reduced to either NH_3 or $NO_{x(g)}$. Additionally, the maximum nitrite concentration observed occurred in the 4V experiment suggesting that nitrite reduction was not as significant compared to the 5 and 10V experiments. These results are also consistent with the findings of the TNT experiments. At maximum concentration, nitrite accounted for approximately 9.2% of the total N in the cathode chamber.

Reaction Rates for Cathodic RDX Transformation – As with TNT transformation, an estimate of reaction rates was determined based on pseudo-first order models fit to the data collected from the cathode chamber of the batch reactor (Table 6). Reaction rates for cell voltages of 10, 5, and 4V were calculated at cathode potentials of <-800 mV SHE. Unlike the TNT reduction, rates of RDX reduction were not dependent on cell voltage. This result suggests mass transfer limitation to the electrode surface. Converting the homogeneous rate constants to heterogeneous constants based on the cell volume and area of the electrode surface yields reaction rates that reflect dependence on surface area of electrode.

Table 6. Reaction Rate Constants for Cathodic Reduction of RDX.

Cell Voltage (V)	Rate constant (min^{-1})	Half-life (min)	Heterogeneous Rate constant ($cm \cdot min^{-1}$)
2	0.0042	130000	0.029
3	0.0039	216000	0.028
4	0.0033	208	0.023
5	3.21×10^{-6}	174	2.25×10^{-5}
10	5.3×10^{-6}	163	3.71×10^{-5}
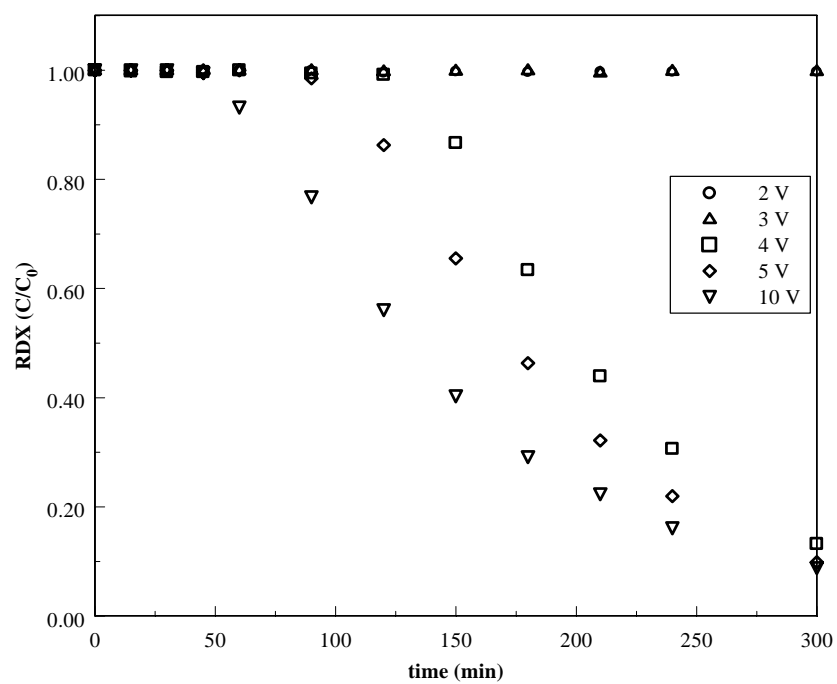
Figure 23. Normalized RDX Concentrations Measured in the Cathode Chamber.
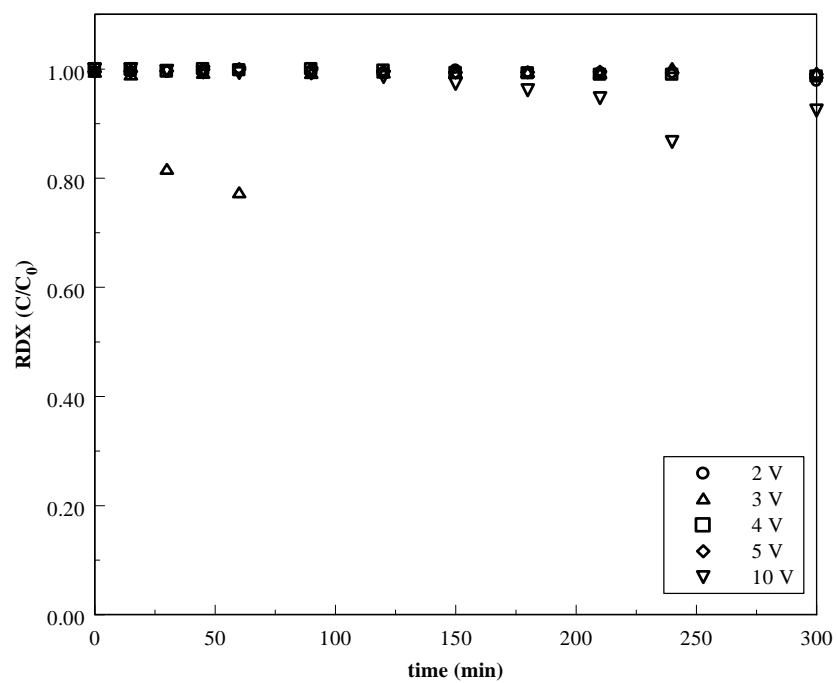
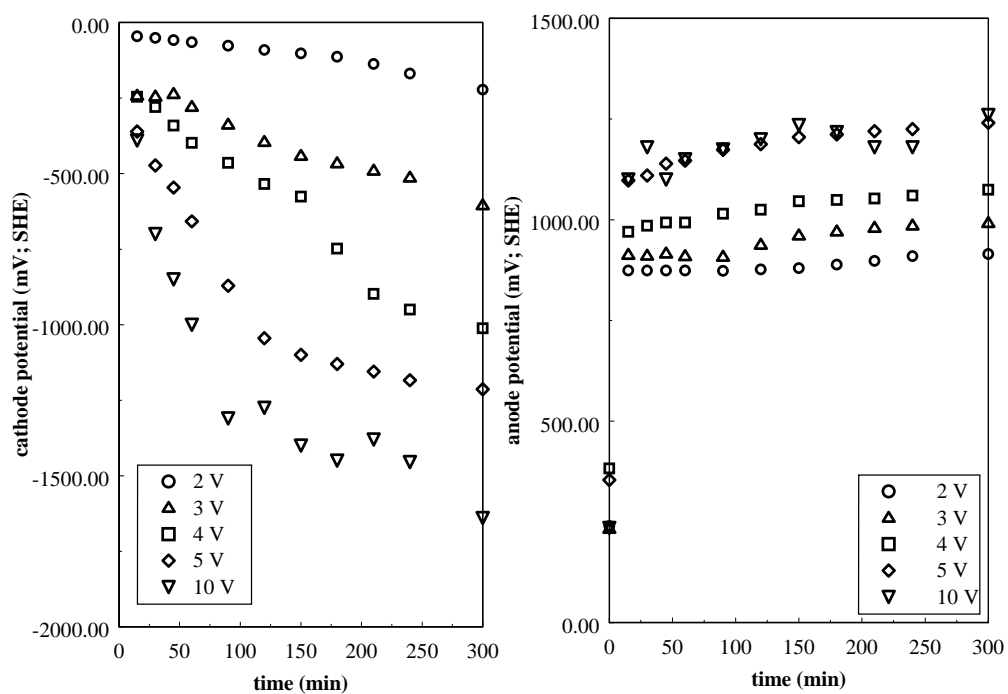**Figure 24. Normalized RDX Concentrations Measured in the Anode Chamber.**
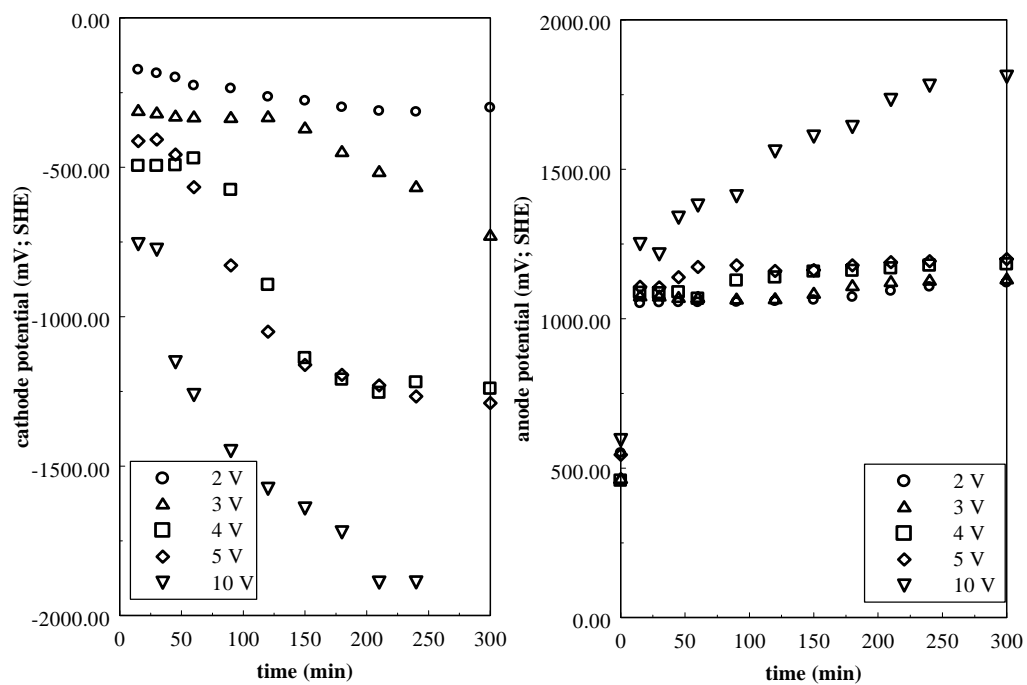
**Figure 25. Cathode (left) and Anode (right) Potentials (SHE) Measured during the RDX Batch Experiments.**
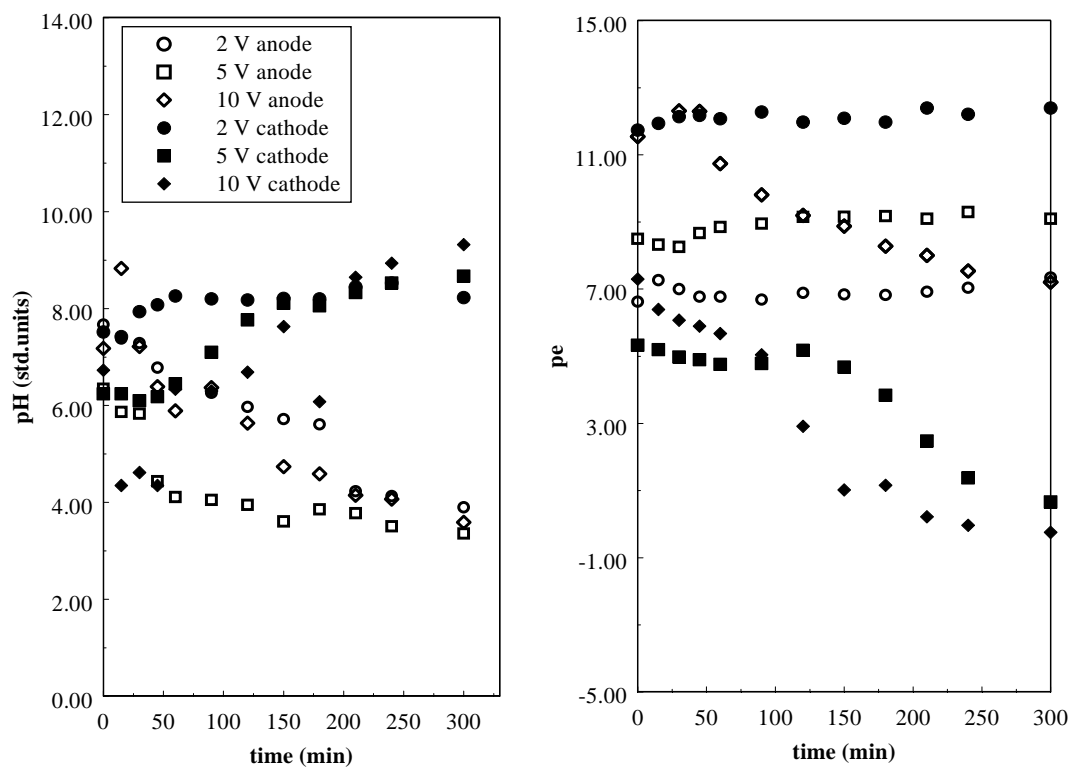
Figure 26. pH and pe Measurements taken in the Anode and Cathode Compartments during the RDX Batch Experiments.
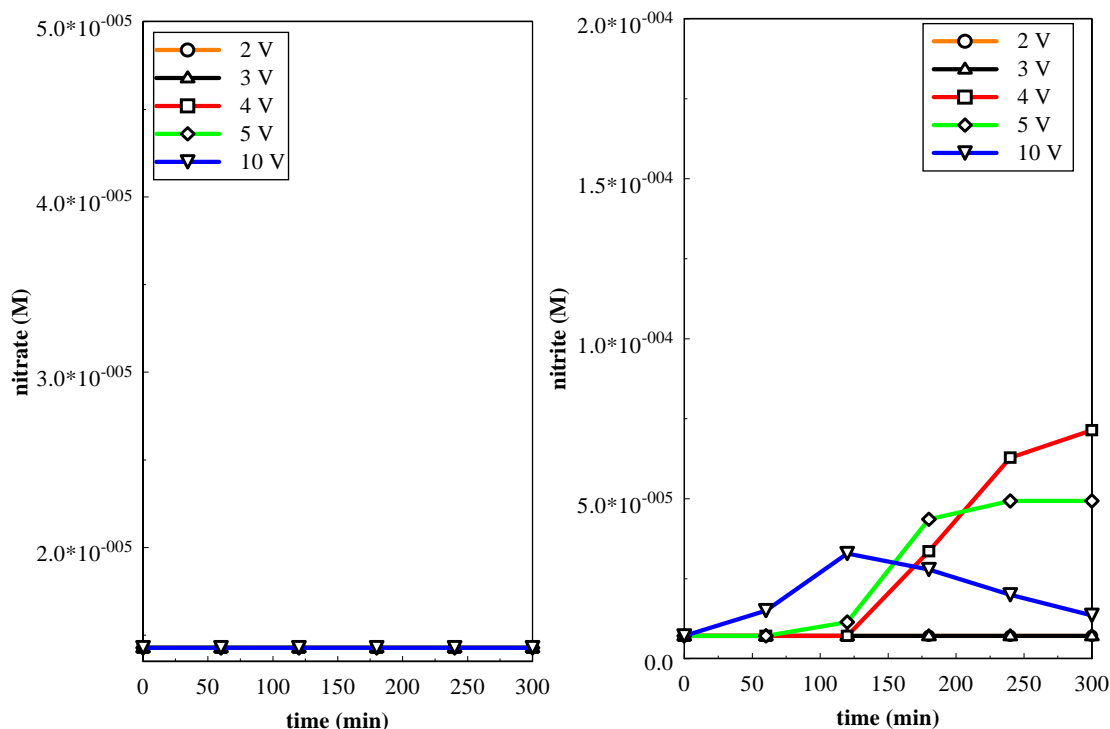
Figure 27. Nitrate (left) and Nitrite (right) Concentrations Measured during the RDX Batch Experiments.

In summary, the Phase 2 batch reactor studies indicated that cathodic reduction is the primary transformation mechanism for both TNT and RDX. Only minor amounts of anodic (oxidative) transformation were observed for both contaminants. Nitrite was generated early in the experiments for bath TNT and RDX suggesting that either denitration or ring cleavage is a rapid process. Electrode potentials necessary for reduction of TNT and RDX were approximately -350 mV SHE and -800 mV SHE respectively.

Phase 2 - Flow-Through Reactor Mass Balance Studies

TNT Results - Flow through reactor studies indicated that 78% of the influent TNT was transformed at the electrode set (Figure 28). Minor amounts of nitrite were observed and nitrate was not observed downstream of the electrode set (Figure 28). Gas generation was not observed at 5V cell potential and was therefore not included in the analysis. Compounds of MW 393, 138, 98, 96, and 78 were identified by LC/MS. Representative mass spectra for the influent and effluent are included below. The difficulty of identification of reaction products and the low concentration of nitrate or nitrite detected, combined with the lack of gas phase products made a mass balance impractical using the data collected. A radiocarbon mass balance study was determined to be the most promising avenue to achieve a mass balance from the column studies.

Cooperative research at the USACE ERDC included mass balance studies using ^{14}C-TNT conducted in an identical flow through reactor (Figure 3). Results indicated approximately approximately 20% of the initial ^{14}C-TNT activity was mineralized to CO_2, approximately 10% remained sorbed to the quartz feldspar sand, and approximately 51% remained in the dissolved phase of which approximately half was unreacted TNT. These results are consistent with those found at CSU, in terms of overall transformation rate. The unidentified fraction of TNT transformation products is an area of further research.
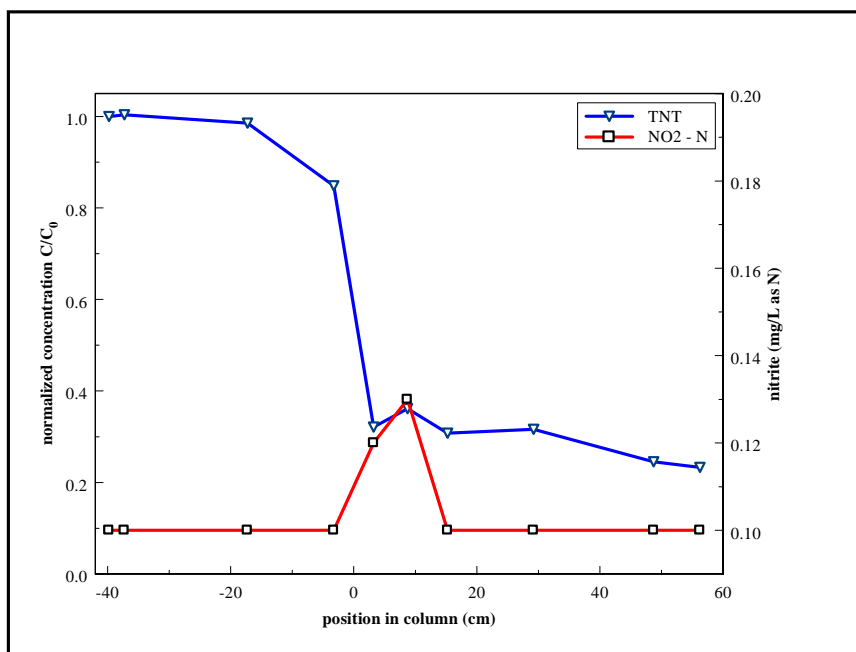
Figure 28. TNT and Nitrite Concentrations as a Function of Position in the Column (0 = position of the Electrode Set).

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Hypothesized partial TNT transformation pathway - Based on data collected in batch and flow-through column experiments, a partial transformation pathway for TNT can be developed (Figure 29). The compounds identified in the pathway have been quantified by HPLC and existing standards or hypothesized from mass spectra. Future work will focus on verifying identification and quantitation of known compounds.

The reaction pathway hypothesized does not include anodic transformation, since to date only minor anodic (oxidative) transformation can be verified. Other potential oxidative pathways (e.g., cathodic formation of Hydrogen Peroxide [H_2O_2]) are under investigation.

The cathodic pathway illustrated in Figure 29 indicates the formation of a compound of molecular weight (MW) 393. This compound has been identified in the cathode chamber of the batch experiments and in the effluent of the flow-through reactor. This compound is hypothesized to be an azoxynitrotoluene compound, although the molecular weight is low relative to the MW 406 reported by others (Junk and Catallo, 1998). It is not clear what fraction of the original TNT forms the MW 393 compound or if adsorption of this compound to the mineral surfaces is responsible for the TNT removal observed in the Phase 1 (proof-of concept) studies. Additional work is required to identify (e.g. LC/MS/MS) and quantify this compound to include it in the overall mass balance. Results from the radiolabeled study suggest that approximately 10% of the influent TNT is transformed to this compound. The pathway resulting in the formation of this compound may be through the amino-dinitrotoluene isomers (Junk and Catallo, 1998) or through diamino-mononitro toluene compounds (Rodgers and Bunce, 2001) although the diamino-mononitro toluene intermediates were not observed in this study.

The hypothesized pathway also includes formation of DNT isomers (MW 182). The formation of DNT is consistent with the formation of nitrite observed in both the batch reactor and the flow-through reactor experiment. The rapid formation of nitrate and nitrite observed in the batch reactor experiments suggests that formation of DNT isomers is an early step in the transformation of TNT, but few other researchers have identified the formation of DNT early in the reductive sequence of TNT. Significant concentrations of DNT (< 50 ug/L) were not observed and it is possible that the nitrate and nitrite measured are not derived from sequential denitration of TNT, but from ring cleavage and rapid transformation of 2,4,6-TNT to low molecular weight products. Regardless, initial 2,4-DNT was also shown to be transformed, consistent with the findings of others (Doppalapudi, et al, 2003; Pehkonen, et al., 1999; Jolas, et al., 2000). From DNT, the pathway likely includes an intermediate compound of MW 152, which was not identified by LC/MS. It is likely that if MW 152 forms, it is short lived. MW 138 was identified by LC/MS, and is likely an amino-hydroxylaminotoluene isomer. It is expected that this is also a short-lived compound and would therefore difficult to detect by MS, but other compounds of MW 138 are not likely to form. Also present in the batch reactor and flow-trough reactor experiments are formation of compounds of MW 98, 96, and 78. MW 98 and 96 would reflect a loss of MW 40 and 42 respectively from MW 138. Formation of MW 98 and 96 would therefore require ring cleavage for formation if MW 138 is an amino-hydroxylaminotoluene isomer. Other possible reductive pathways

involving the formation of the amino-dinitrotoluene isomers (MW 197- identified by LC/MS), the diamino-nitrotoluene isomers (MW 167 – not identified by LC/MS) and triaminotoluene (MW 137 – not identified by LC/MS) are not well supported by the existing data, although work by others suggests that azoxynitrotoluene formation may include triaminotoluene (TAT) as an intermediate (Hawari, et al., 1998).

It is important to note that the evidence provided for the hypothesized reaction pathway is based on observed mass spectra. It is possible that alternate pathways (that do not result in accumulation of compounds that can be observed by mass spectrometry) are also followed.
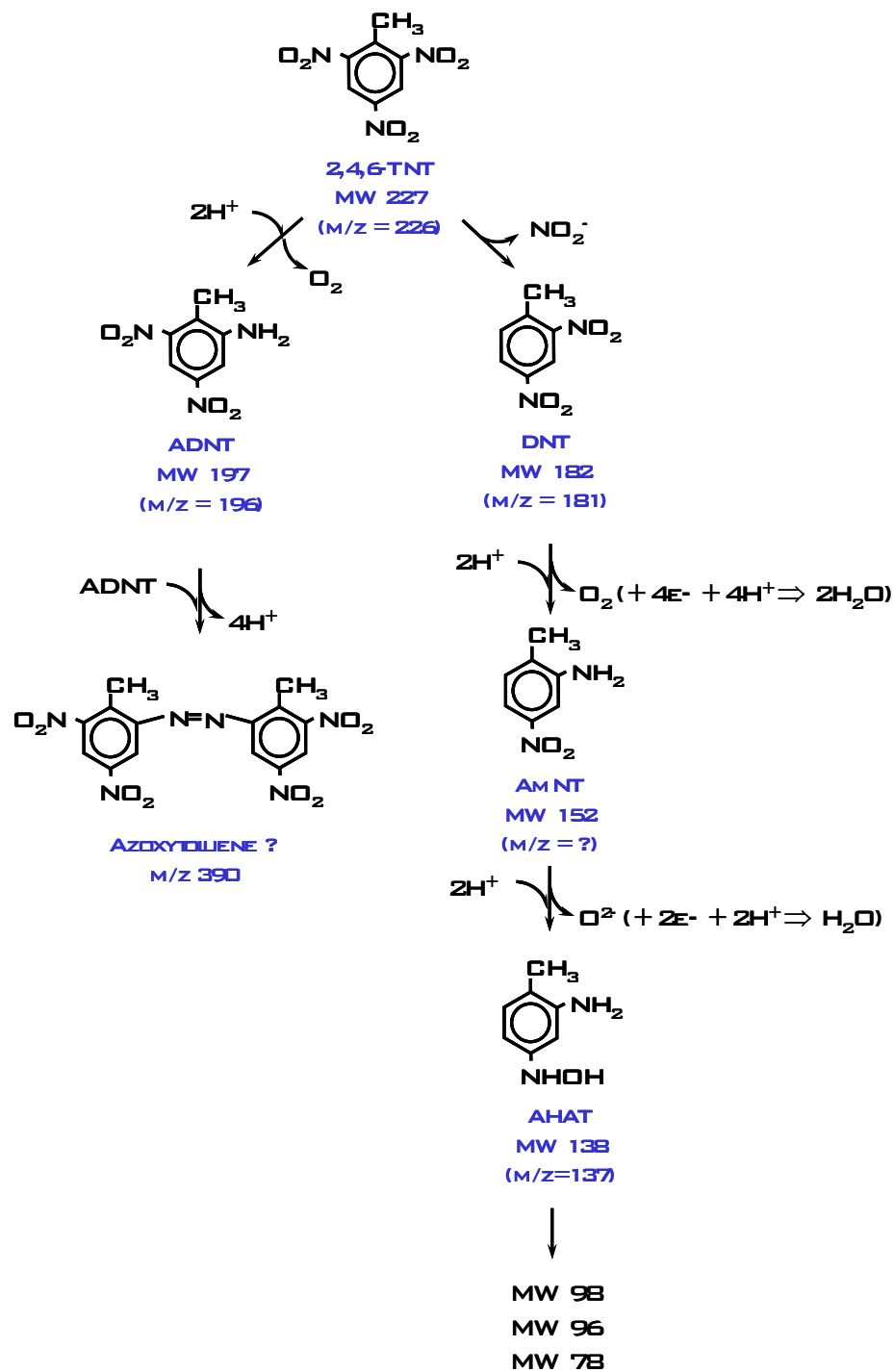
Figure 29. Hypothesized Partial Pathway for Electrolytic Reduction of TNT.
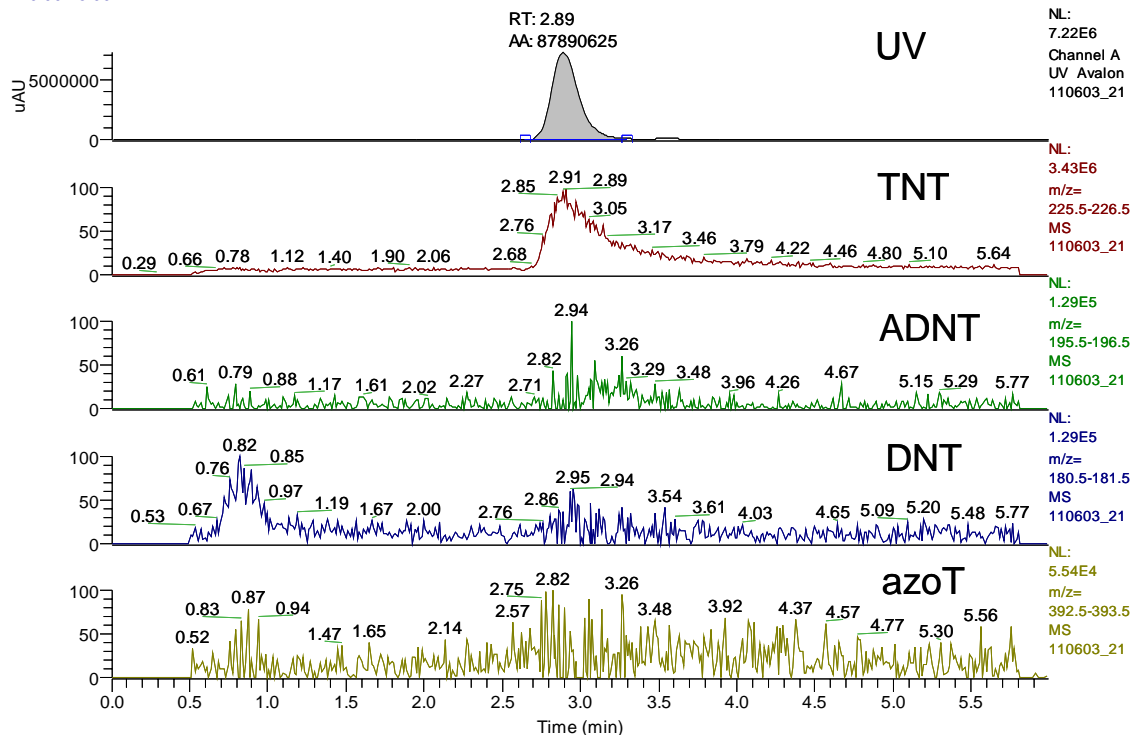
Figure 30. TNT Chromatogram and Mass Specific m/z 226 (2nd from top) at Time t = 0. Chromatograms for ADNT m/z 196 (3rd from top), DNT m/z 181 (4th from top) and Azoxytoluene m/z 393 (bottom) are also included.
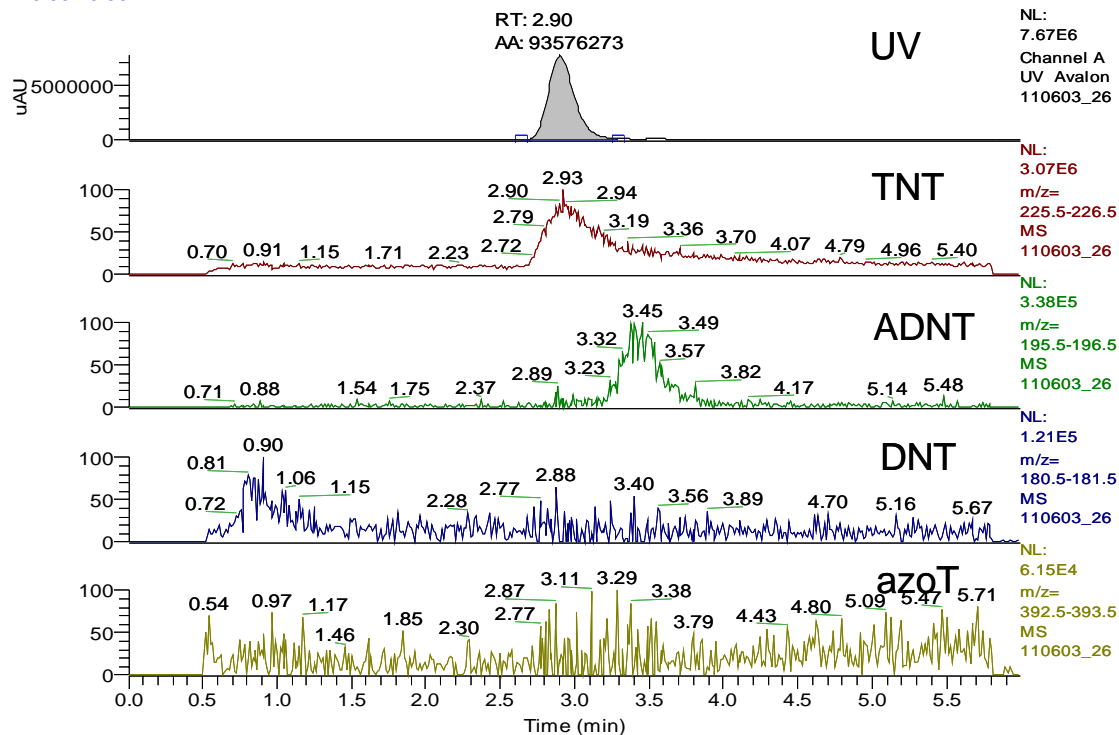
Figure 31. TNT Chromatogram and Mass Specific m/z 226 (2nd from top) at Time t = 60 minutes. Chromatograms for ADNT m/z 196 (3rd from top), DNT m/z 181 (4th from top) and Azoxytoluene m/z 393 (bottom) are also included. Formation of ADNT is Evident.
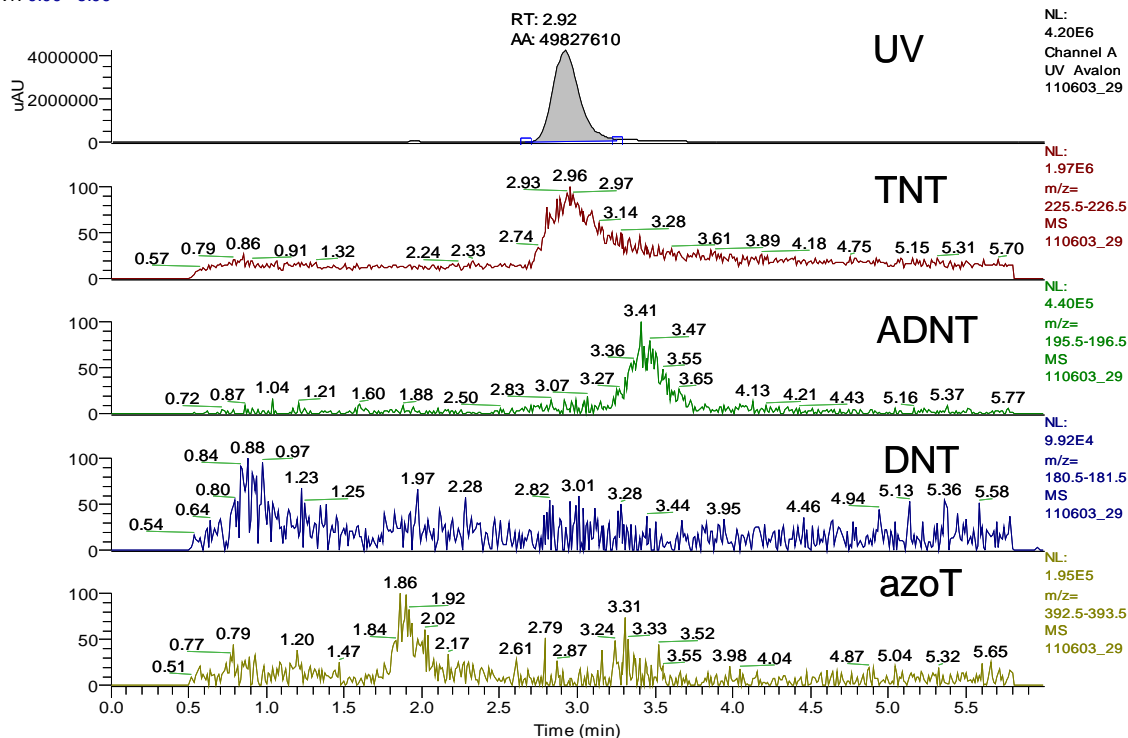
Figure 32. TNT Chromatogram and Mass Specific m/z 226 (2nd from top) at Time t = 120 minutes. Chromatograms for ADNT m/z 196 (3rd from top), DNT m/z 181 (4th from top) and Azoxynitrotoluene m/z 393 (bottom) are also included. ADNT is Present and Formation of Azoxynitrotoluene is Evident.
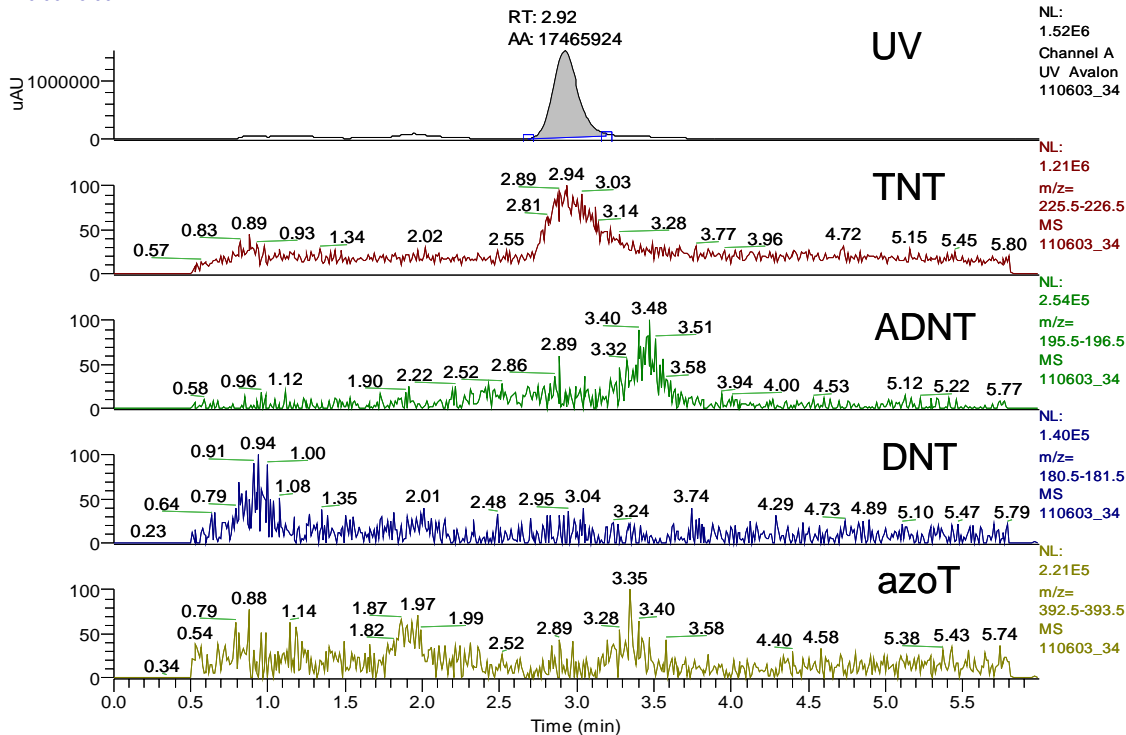
Figure 33. TNT Chromatogram and Mass Specific m/z 226 (2nd from top) at Time t = 180 minutes. Chromatograms for ADNT m/z 196 (3rd from top), DNT m/z 181 (4th from top) and Azoxynitrotoluene m/z 393 (bottom) are also included. ADNT and Azoxynitrotoluene are Evident.
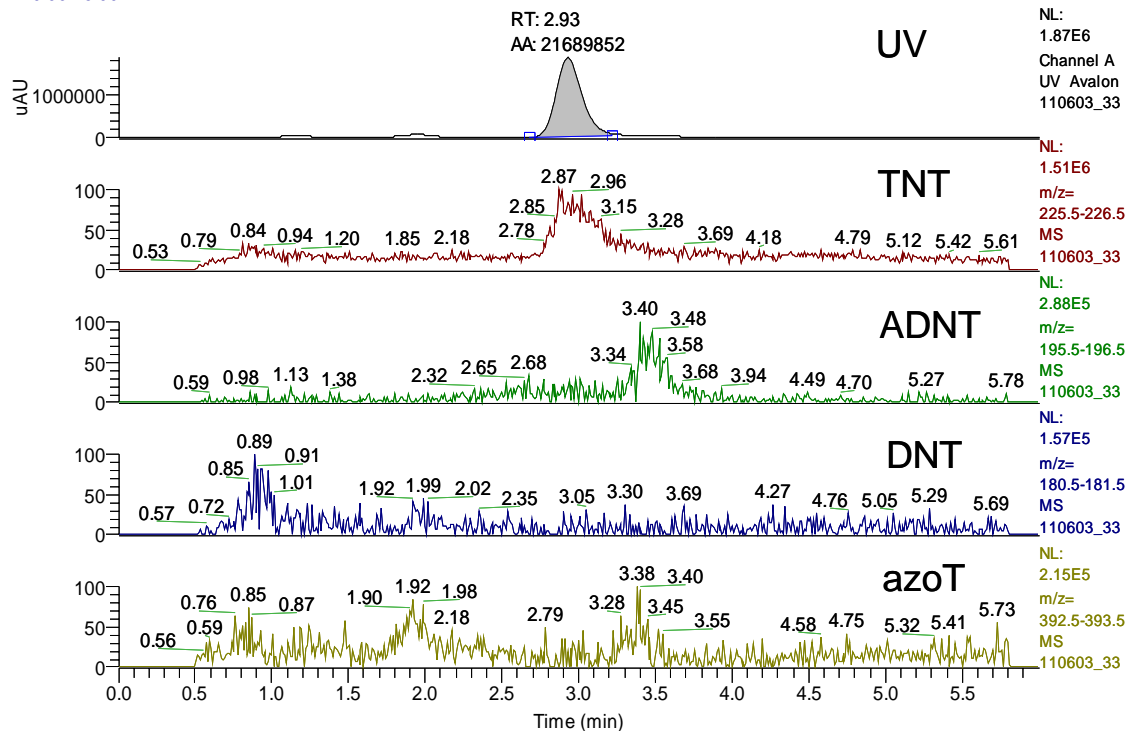
Figure 34. TNT Chromatogram and Mass specific m/z 226 (2nd from top) at Time t = 300 minutes. Chromatograms for ADNT m/z 196 (3rd from top), DNT m/z 181 (4th from top) and Azoxynitrotoluene m/z 393 (bottom) are also included. ADNT and Azoxynitrotoluene are evident.

Phase 2 - Flow-Through Reactor Mass Balance Studies

RDX Results - Flow through reactor studies indicated that approximately 68% of the influent RDX was transformed at the electrode set (Figure 35). Transformation of RDX appeared to continue downstream of the electrode set reaching a final transformation of approximately 77% of the influent RDX. This overall transformation rate is consistent with the findings of the radiolabeled study conducted at the USACE ERDC.

Minor amounts of nitrite were observed and nitrate was not observed downstream of the electrode set (Figure 36). Minor gas generation was observed at 5V cell potential. Due to the small volume of gas generated, analysis was limited to nitrogen oxides which were found to be present. This result is consistent with the results of other researchers who have identified N_2O as a product of RDX mineralization (Bonin, et al., 2004). Other products identified by LC/MS were compounds hypothesized to be MNX, DNX, TNX and nitramide

Cooperative research at the USACE ERDC included mass balance studies using ^{14}C RDX conducted in an identical flow through reactor (Figure 37). Results indicated approximately 20% mineralization of RDX and formation of non-nitroso products (approximately 43%). Approximately 29% of the initial RDX was unreacted. The overall transformation rate and absence of nitroso-substituted intermediates is consistent with the flow-through studies conducted at CSU.

Figure 35. Normalized RDX Concentration as a Function of Position in the Column (0 = position of the Electrode Set).

Figure 36. Nitrite and Nitrate Concentrations as a Function of Position in the Column (0 = position of the Electrode Set).

Hypothesized partial RDX transformation pathway - Based on data collected in batch and flow-through column experiments, a partial transformation pathway for RDX can be developed (Figure 37). The compounds identified in the pathway have been quantified by HPLC and existing standards or hypothesized from mass spectra.
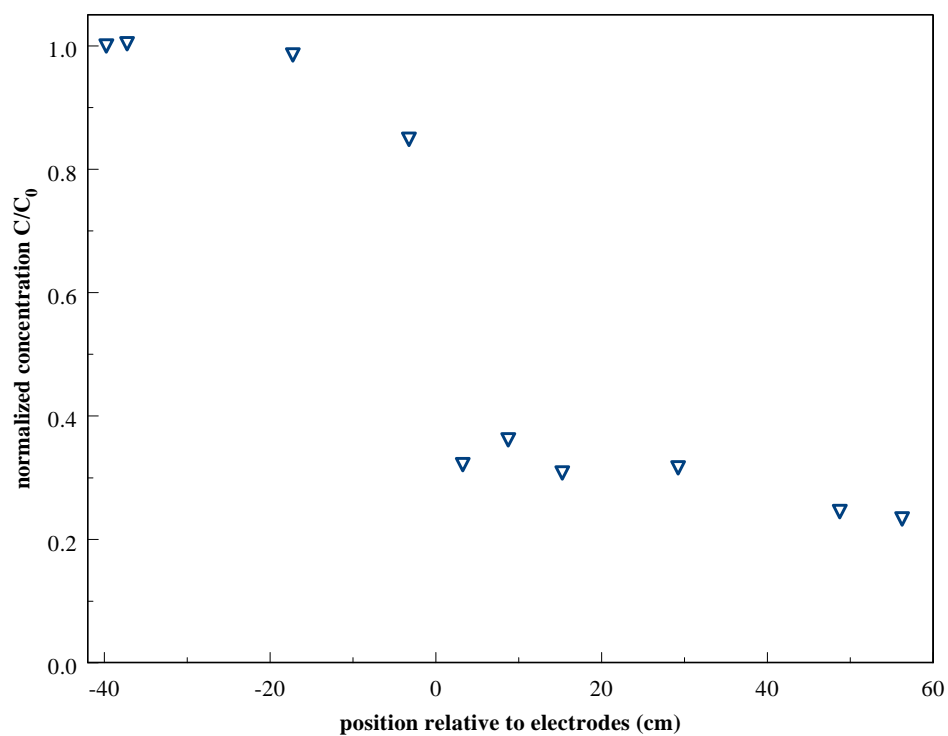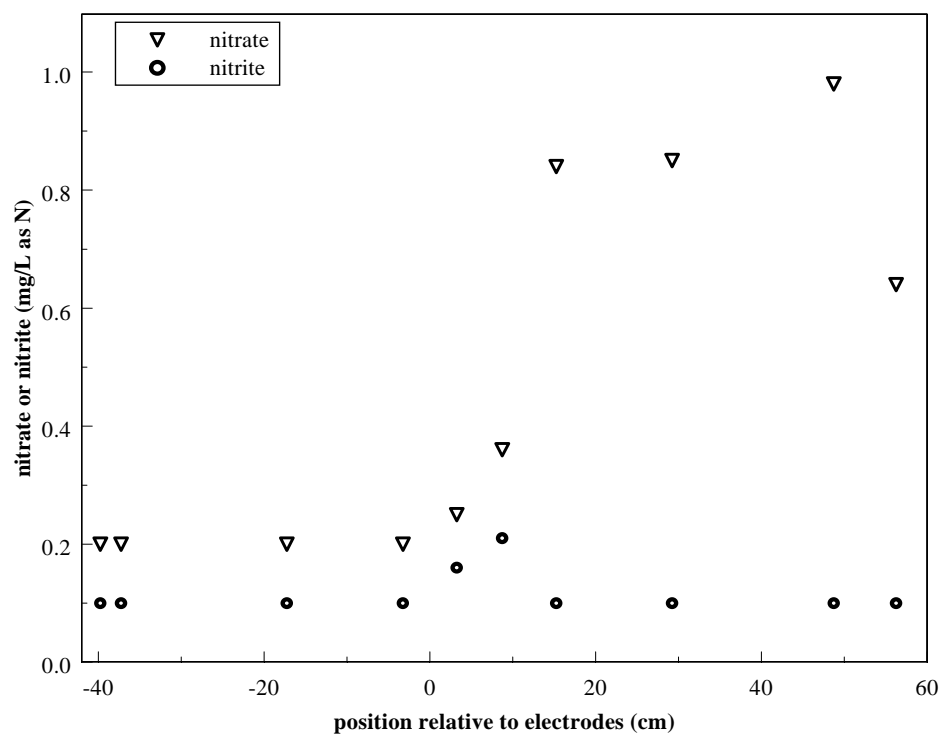
As with TNT, the reaction pathway hypothesized does not include anodic transformation, since to date only minor anodic (oxidative) transformation has been observed.

The reductive pathway illustrated in Figure 37 follows the work by others (e.g. Bonin, et al., 2004; Groom, et al., 2001) and indicates the formation of the nitroso-substituted intermediates (MNX, DNX and TNX). These compounds are present only in trace amounts making quantition difficult. Figure 38 - Figure 47 provides evidence for this pathway. Combined with the ^{14}C-RDX findings, suggest that if this is the primary pathway, the nitroso compounds are readily transformed and not accumulated.

The hypothesized pathway also includes formation of nitramide (MW 62, m/z = 61). The formation of nitramide is consistent with ring cleavage and formation of formaldehyde (not included in this analysis). The formation of nitrite observed may be the result of the formation of nitramide and not denitration in an early transformation step. If early denitration occurred a compound of MW 176 would be formed (there is evidence that a compound of MW 176 is formed, but further verification is necessary). If this alternate pathway occurs, it is likely that ring cleavage will occur rapidly resulting in additional nitrite and nitramide formation.

It has been widely reported that the reductive pathway for RDX transformation includes methylenedinitramine (MDNA). Formation of this compound was not observed during this study, but its presence is reported to be transient. Other potential intermediates reported by others include hydroxylamine compounds that were also not observed during this study.

Final products of RDX reduction are likely nitramide which is m/z 61 (Figure 37) and formaldehyde which was not included in this analysis. Quantification of formaldehyde is a current focus of our research.

It is important to note that the evidence provided for the hypothesized reaction pathway is based on observed mass spectra. It is possible that alternate pathways (that do not result in accumulation of compounds that can be observed by mass spectrometry) are also followed.

Evaluation of the RDX transformation pathway is complicated by the presence of HMX and a compound of m/z 161 (e.g. Figure 38). It is not clear if the ultimate reduction products observed are the result of RDX or HMX transformation. Note that approximately 80% of the initial HMX present was transformed during the 300 minute batch reactor study study.
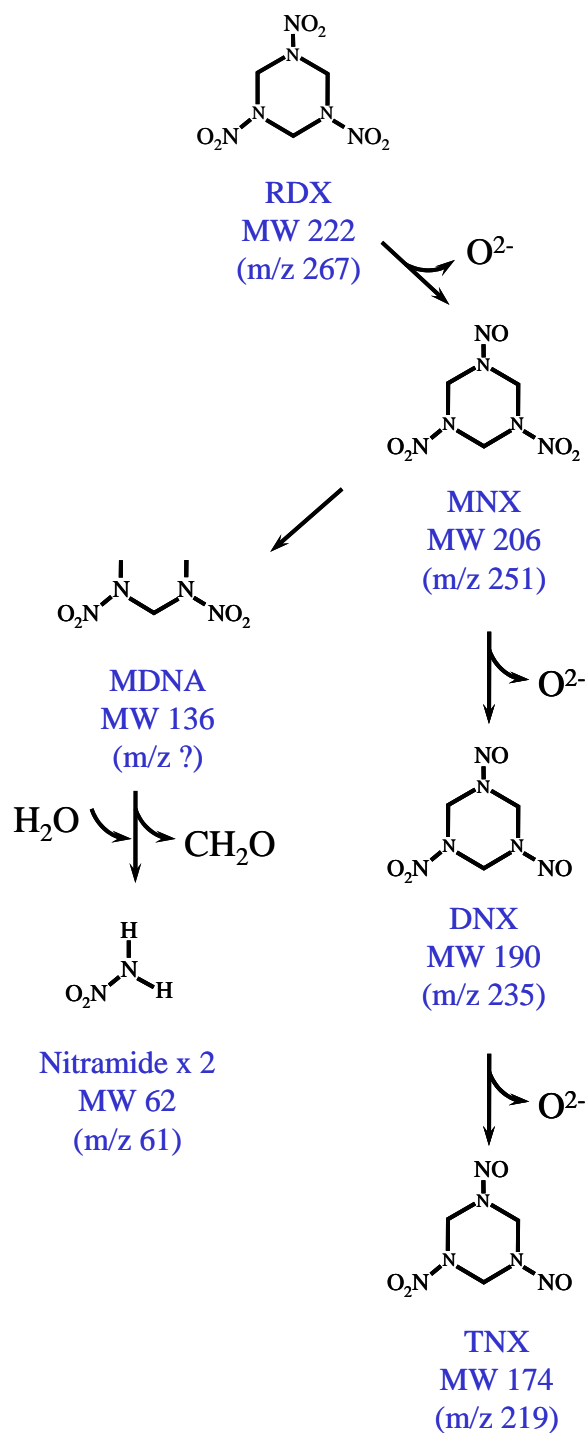
Figure 37. Hypothesized Partial Transformation Pathway for Cathodic Reduction of RDX. All of the Compounds in the Above Diagram have been Identified in this Study with the exception of MDNA which is a Hypothesized Intermediate.

Figure 38. Chromatograms from the Catholyte Collected at t = 0 minutes (initial conditions) in the Phase 2 Batch Reactor Studies at 5V Cell Potential. UV Chromatogram (top) Indicates Presence of RDX (RT 4.60), HMX (RT 3.39) and a Compound of m/z 161. Specific m/z Mass Chromatogram (2nd from top) Indicates RDX at m/z 267 (m+46-H). Specific m/z Mass Chromatogram (3rd from top) Indicates HMX at m/z 341 (m+46-H). Specific m/z Mass Chromatogram (bottom) Indicates Unidentified Compound of m/z 161 Present in the catholyte at t = 0.

Figure 39. Chromatograms from the Catholyte Collected at t = 60 minutes in the Phase 2 Batch Reactor Studies at 5V cell potential. UV Chromatogram (top) Indicates Presence of RDX (RT 4.60), HMX (RT 3.39) and the Compound of m/z 161. Little Transformation has Occurred at t = 60 minutes.
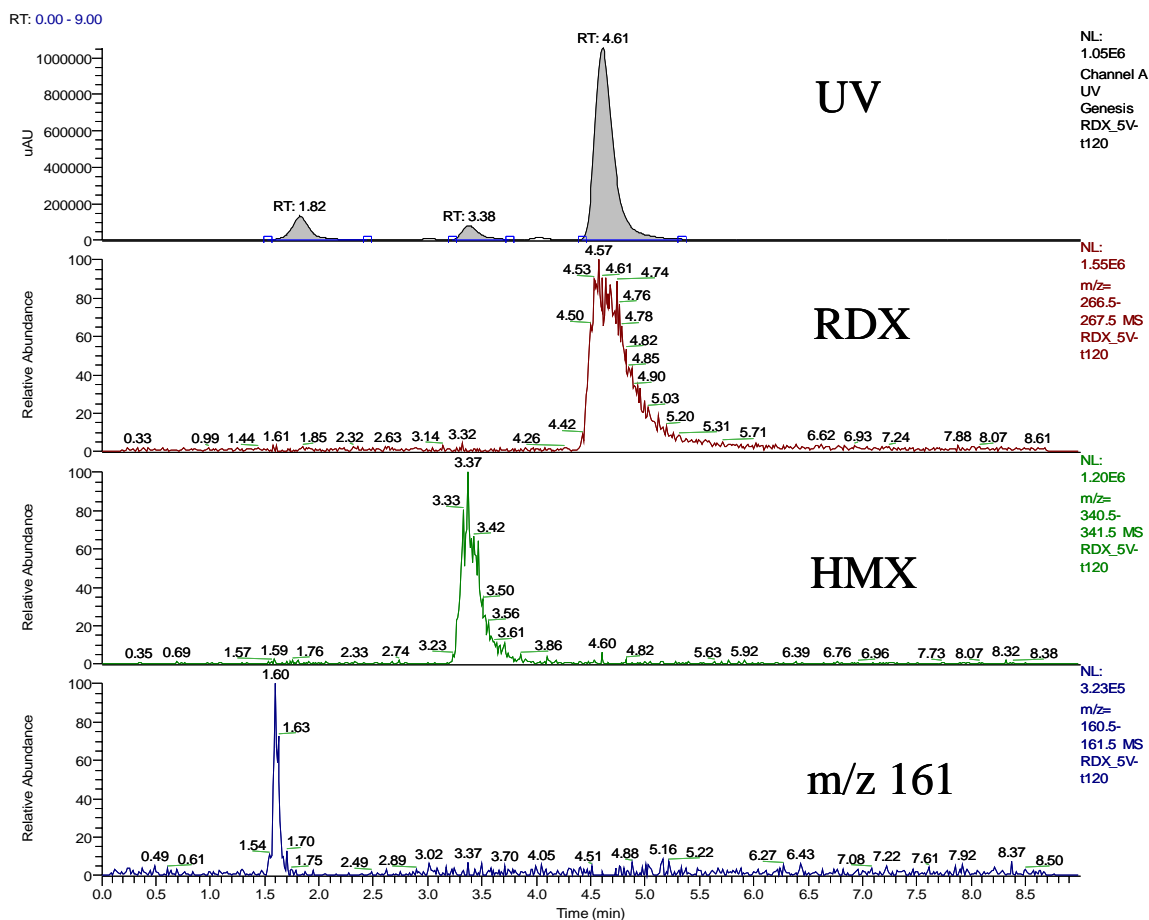
Figure 40. Chromatograms from the Catholyte Collected at t = 120 minutes in the Phase 2 Batch Reactor Studies. UV Chromatogram (top) Indicates Presence of RDX (RT 4.60), HMX (RT 3.39) and the Compound of m/z 161. Little Transformation of RDX or HMX has Occurred at t = 120 minutes.

Figure 41. Chromatograms from the Catholyte Collected at t = 120 minutes in the Phase 2 Batch Reactor Studies at 5V Cell Potential. UV Chromatogram (top) Indicates Presence of RDX (RT 4.60), HMX (RT 3.39) and the Compound of m/z 161 (RT 1.82). Approximately 14% of the Initial RDX has been Transformed. The Formation of MNX (2nd from top), DNX (3rd from top) and TNX (bottom) is Evident from the Specific m/z Mass Chromatograms.

Figure 42. Chromatograms from the Catholyte Collected at t = 180 minutes in the Phase 2 Batch Reactor Studies at 5V Cell Potential. UV Chromatogram (top) Indicates Presence of RDX (RT 4.60), HMX (RT 3.39) and the Compound of m/z 161. Approximately 54% of the Initial RDX has been Transformed.

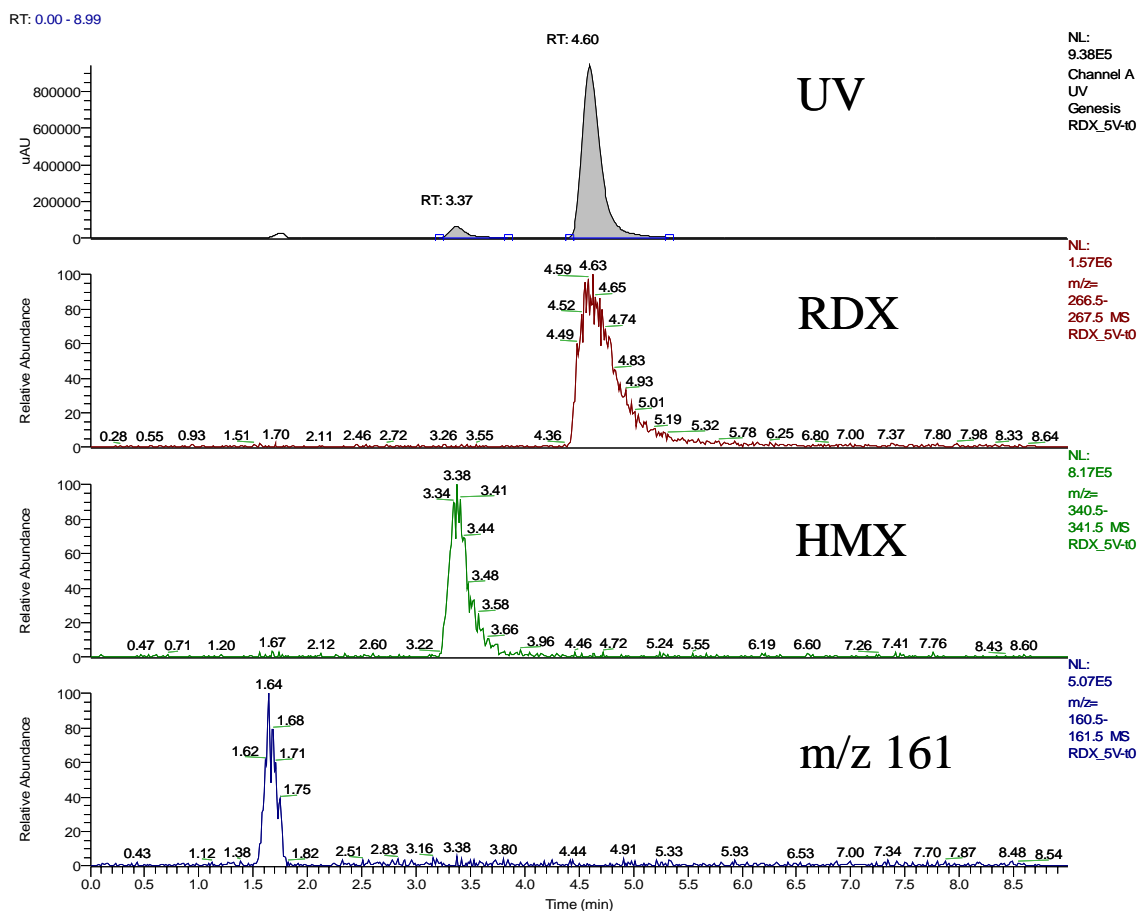**Figure 43. Chromatograms from the Catholyte Collected at t = 180 minutes in the Phase 2 Batch Reactor Studies at 5V Cell Potential. UV Chromatogram (top) Indicates Presence of RDX (RT 4.60), HMX (RT 3.39) and the Compound of m/z 161 (RT 1.82). RDX Transformation of Approximately 54% has Occurred; the Formation of MNX (2nd from top), DNX (3rd from top) and TNX (bottom) is Evident from the Specific m/z Mass Chromatograms.**
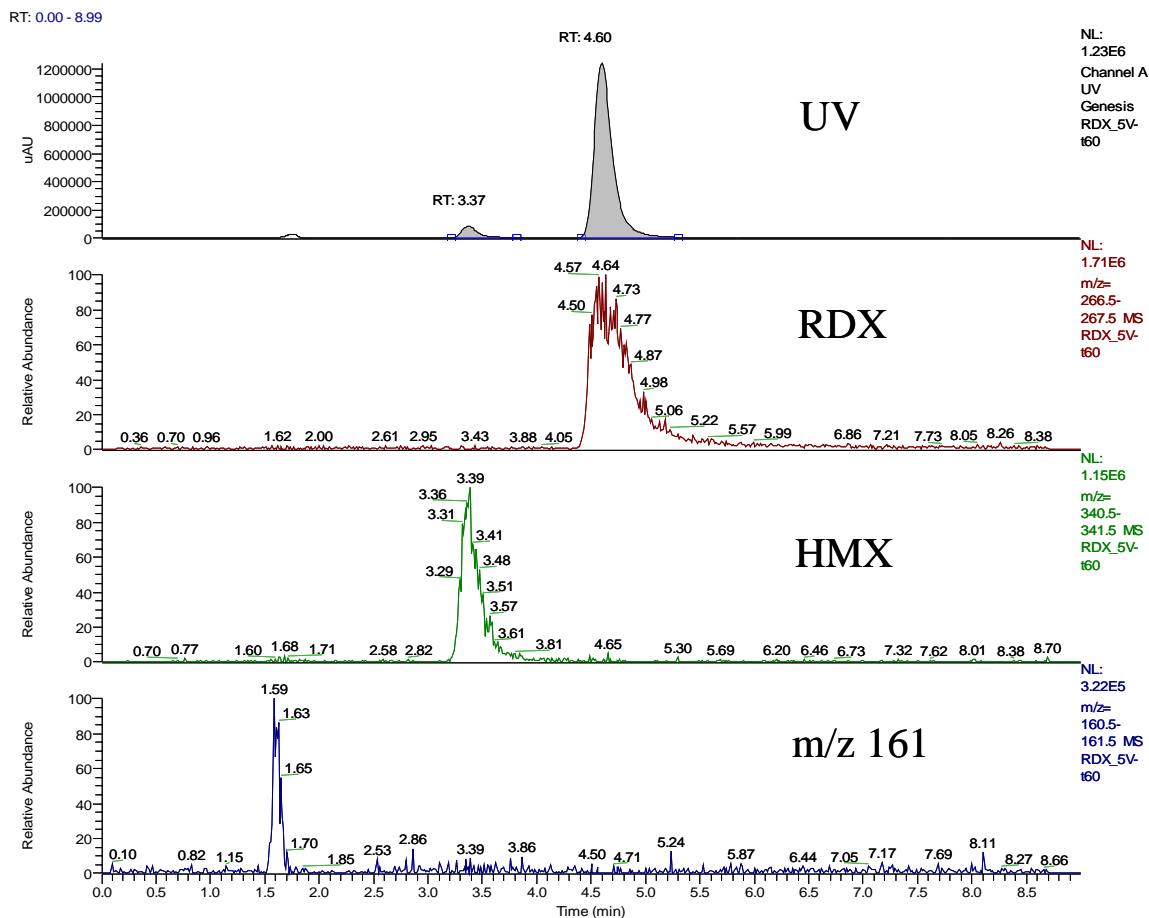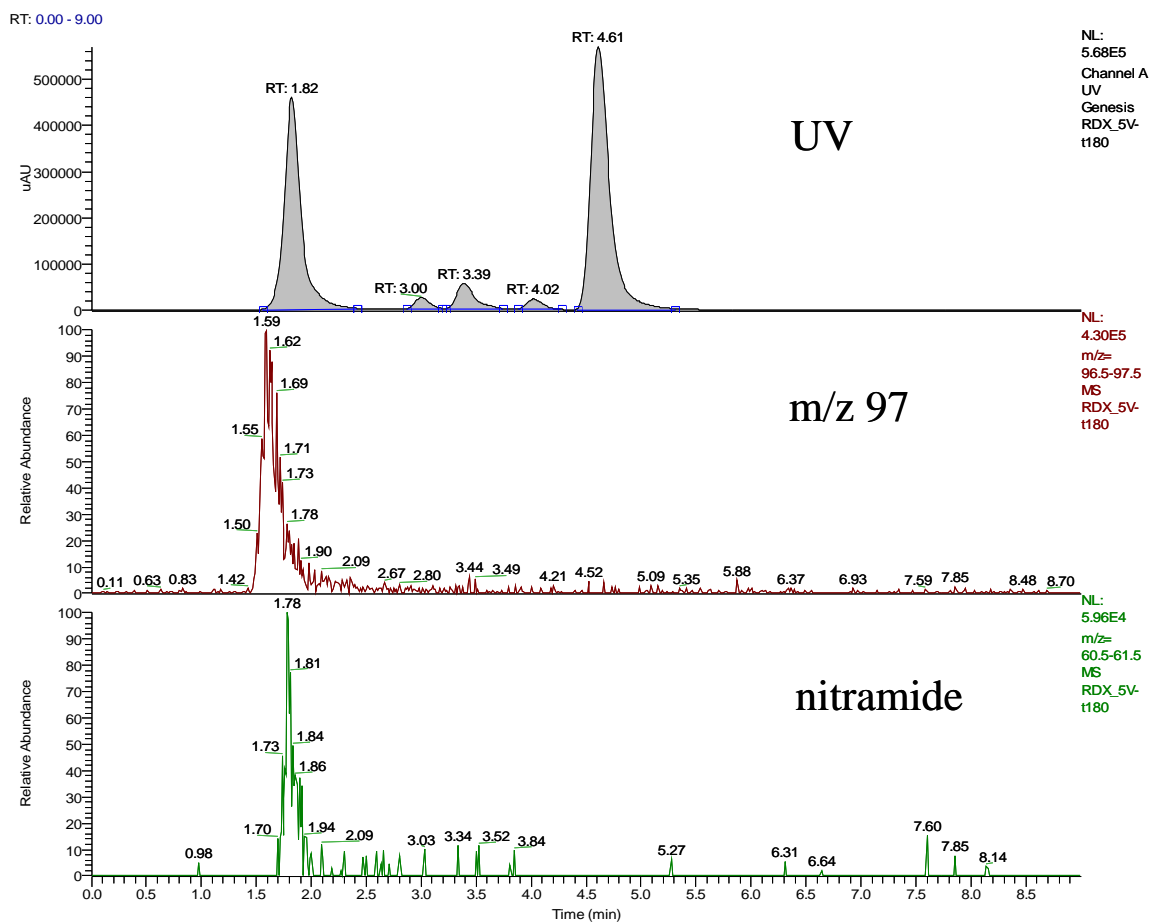
Figure 44. Chromatograms from the Catholyte Collected at t = 180 minutes in the Phase 2 Batch Reactor Studies at 5V Cell Potential. UV Chromatogram (top) Indicates Presence of RDX (RT 4.60), HMX (RT 3.39) and the Compound of m/z 161 (RT 1.82). RDX Transformation of Approximately 54% has Occurred; the Formation of m/z 97 (2nd from top) and Nitramide (bottom) is Evident from the Specific m/z Mass Chromatograms. Note that these Compounds are coeluted with m/z 161 at approximately RT 1.8.
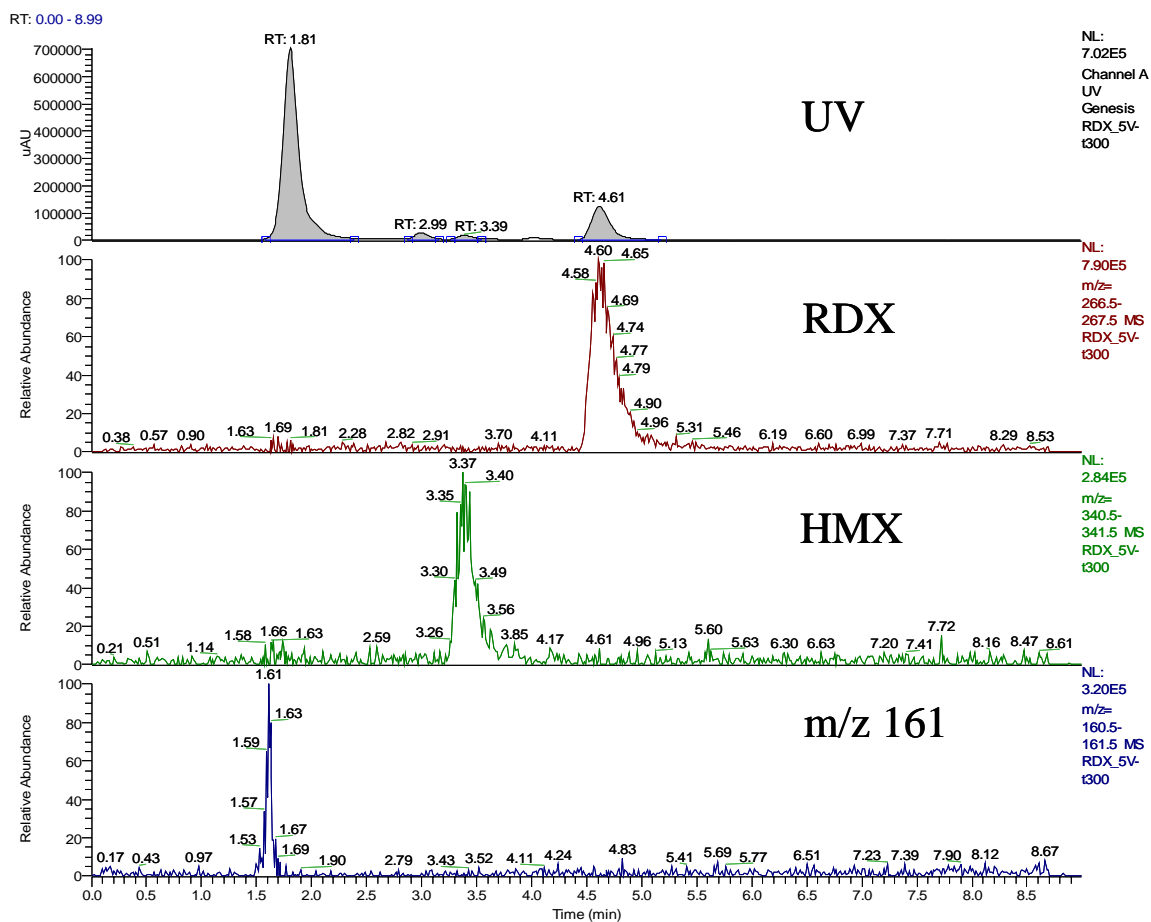
Figure 45. Chromatograms from the Catholyte Collected at t = 300 minutes in the Phase 2 Batch Reactor Studies at 5V Cell Potential. UV Chromatogram (top) Indicates Presence of RDX (RT 4.61), HMX (RT 3.39), and the Compound m/z 161 (RT 1.81). Approximately 90% of the Initial RDX has been Transformed.
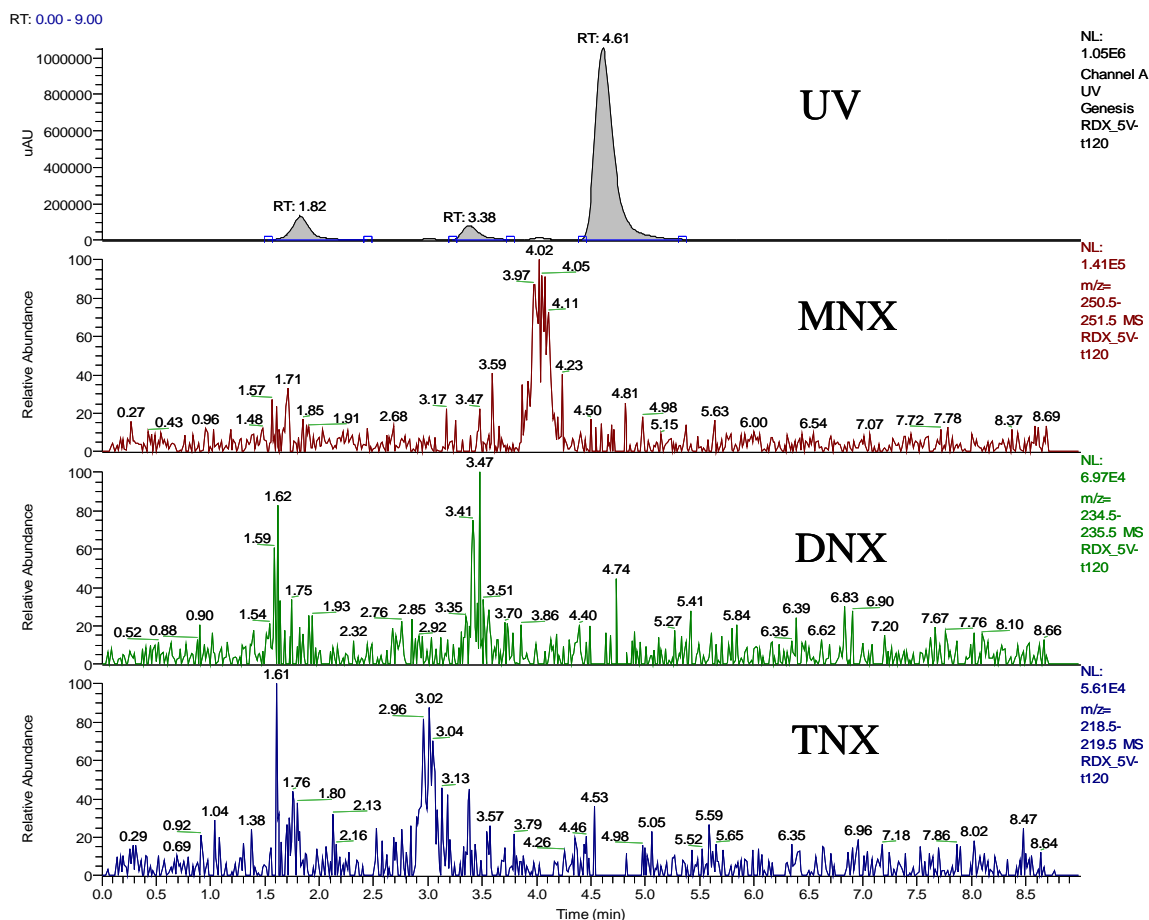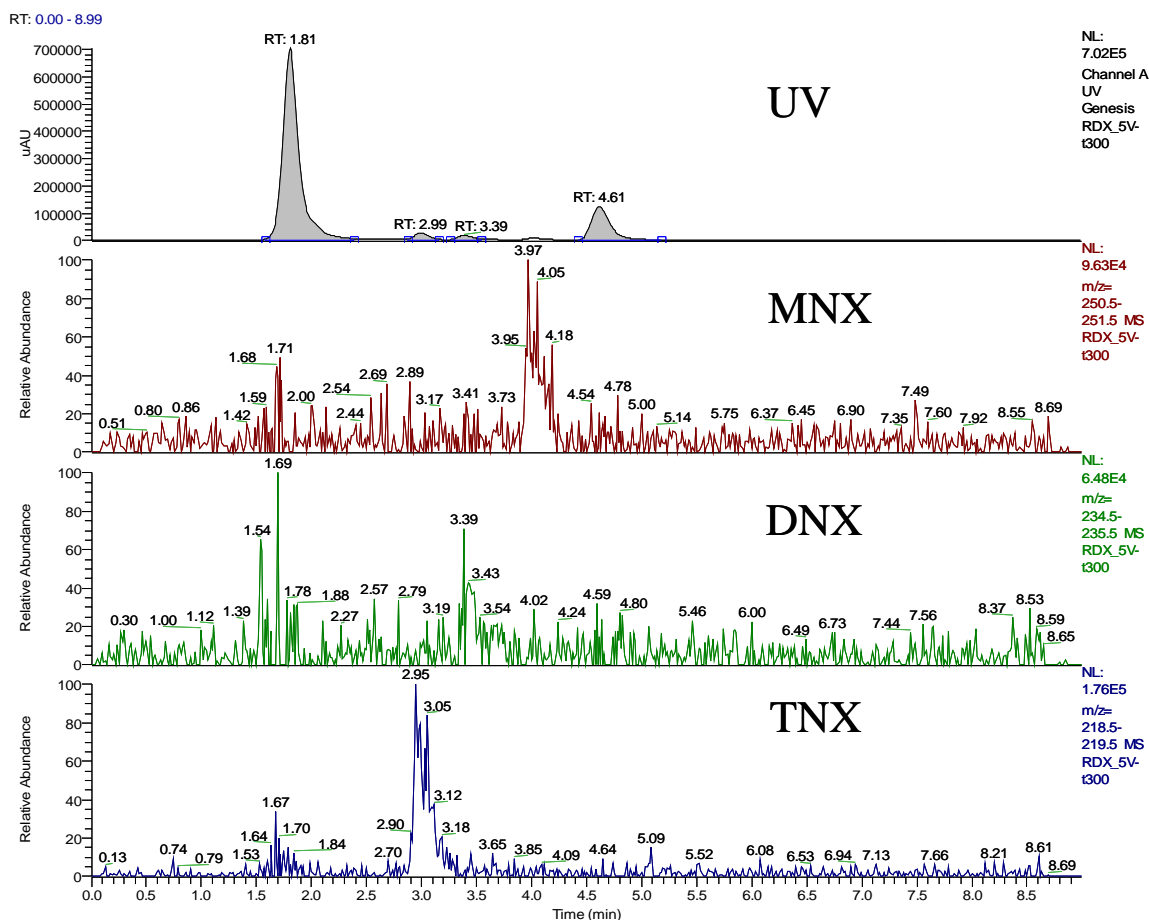
Figure 46. Chromatograms from the Catholyte Collected at t = 300 minutes in the Phase 2 Batch Reactor Studies at 5V Cell Potential. UV Chromatogram (top) Indicates Presence of RDX (RT 4.63), HMX (RT 3.39). Approximately 90% of the Initial RDX has been Transformed. MNX (2nd from top) is Present but at a Significantly Lower Concentration than at t = 180 minutes (approximately 25% of the t = 180 concentration), DNX is not Clearly Present (3rd from top) and TNX is also Present (bottom), but at a Slightly Lower Concentration than at t = 180 minutes.
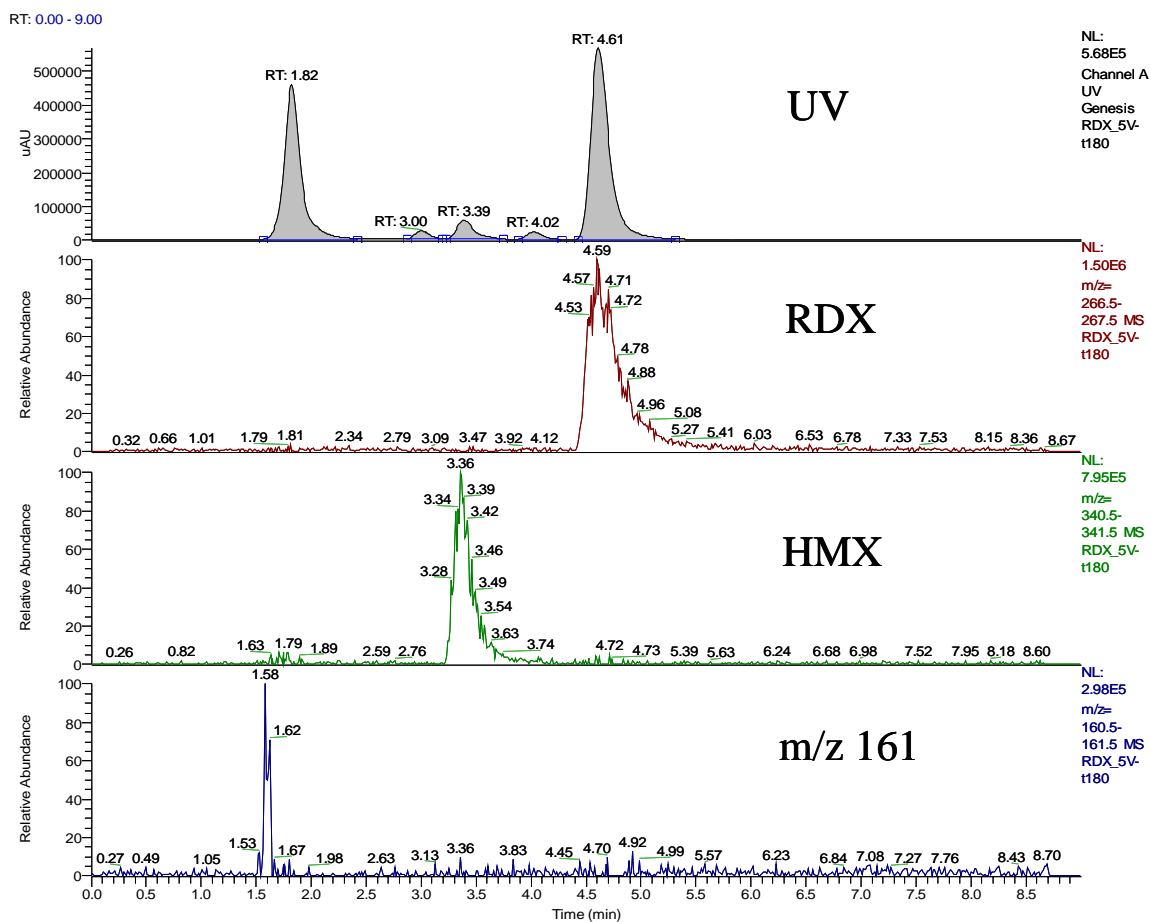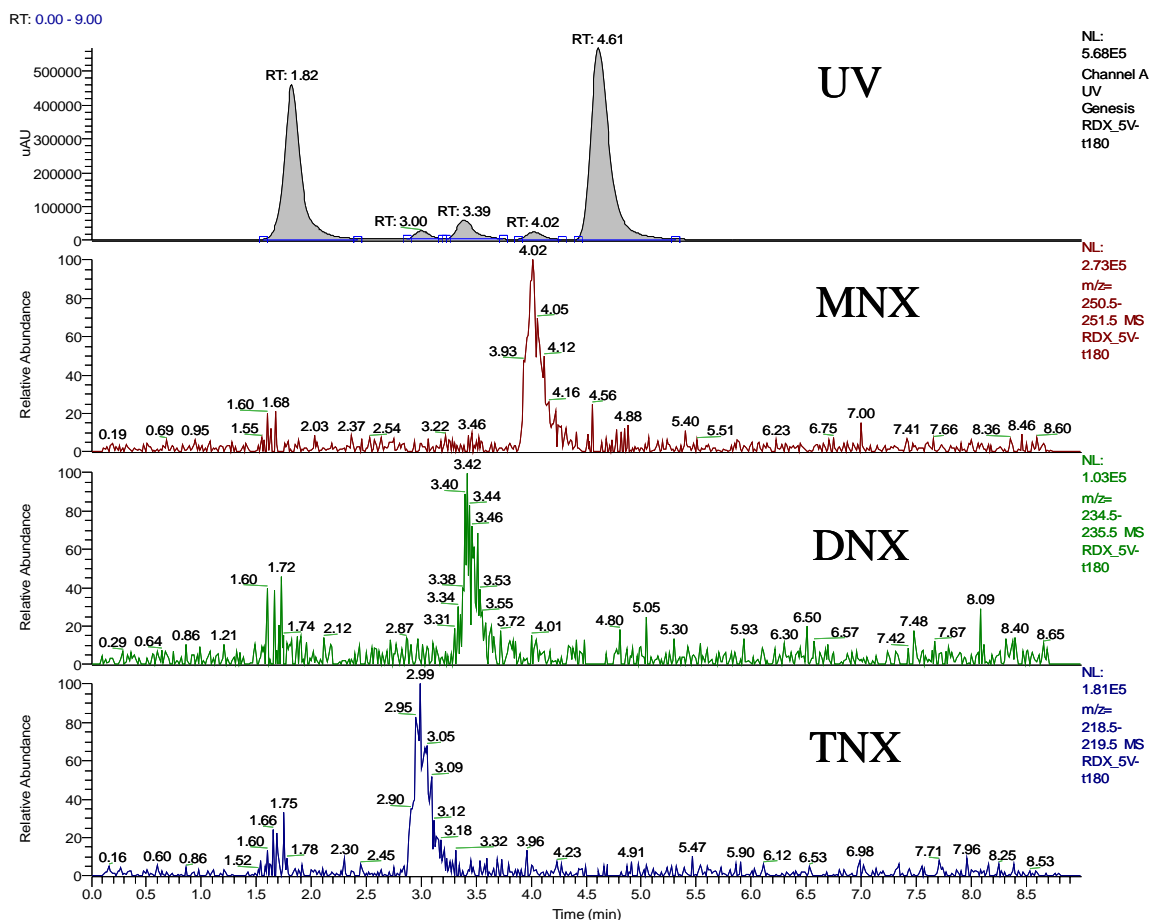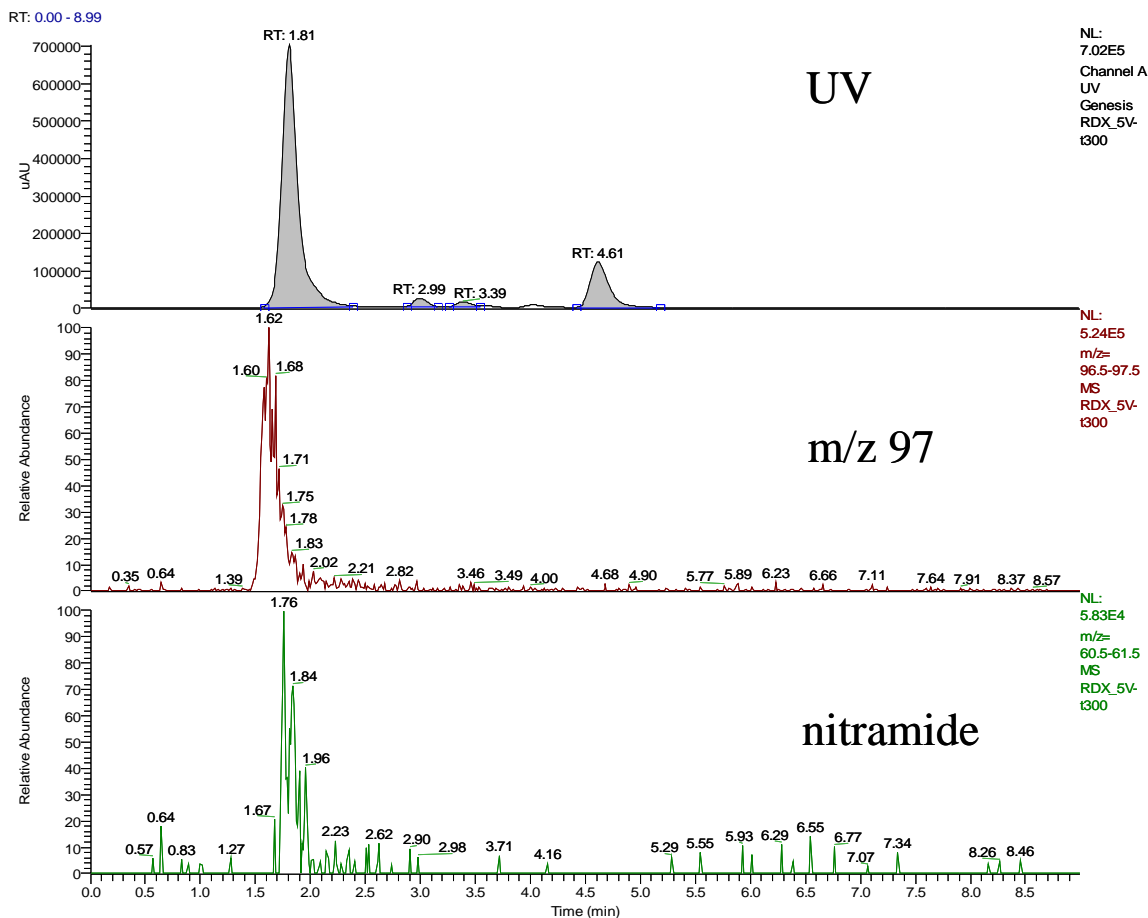
Figure 47. Chromatograms from the Catholyte Collected at t = 300 minutes in the Phase 2 Batch Reactor Studies at 5V Cell Potential. UV Chromatogram (top) Indicates Presence of RDX (RT 4.63), HMX (RT 3.39). Approximately 90% of the Initial RDX has Been Transformed. Compound of m/z 97 is Clearly Evident (2nd from top) at a Concentration slightly higher than at t = 180 minutes and nitramide is present at a slightly lower concentration than at t = 180 minutes (bottom).

In summary, the Phase 2 mass balance studies indicated that overall approximately 70% of the influent RDX was transformed. Approximately 20 % of the initial RDX was completely mineralized using a single electrode set. For RDX, approximately 48% of the initial was transformed to non-nitroso products. Results suggest that these products are likely formaldehyde and nitramide. Approximately 25% of the initial RDX was unreacted.

For TNT, approximately 20% of the initial mass was mineralized. Approximately 10% of initial TNT was adsorbed to the sand matrix, likely as azoxynitrotoluene. Approximately, 25% of the initial TNT was unreacted in a single electrode set. The remaining mass was unaccounted for.

The results between the CSU and ERDC laboratory column studies are consistent. The discrepancy between the Phase 1 values and the Phase 2 results is likely the length of the experiments. Over time, contaminant concentrations downstream of the electrodes decreased, resulting in a higher calculated removal. The Phase 1 experiments were conducted over a much longer period than the Phase 2 experiments.

Hypothesized transformation pathways for RDX likely follow pathways published in recent literature. From RDX, it is likely that MNX, DNX and TNX are formed and rapidly transformed to MEDINA which is then hydrolyzed to nitramide and formaldehyde. Nitrite and nitrogen oxide gases are also formed.

The hypothesized transformation pathway for TNT includes formation of ADNT isomers likely followed by polymerization to azoxynitrotoluene. An alternate pathway may include denitration followed by successive reduction to nitrite.

Quality Assurance-Quality Control (QA/QC)

QA/QC measures included replicate extractions, split analysis, matrix blank analysis, and calibration checks for analytical instrumentation.

For the Phase 1 studies, replicate extractions were conducted to evaluate extraction precision. The replicate extractions consisted of splitting a sample and extracting each subsample. Each replicate extractant was analyzed independently. Replicate extractions were conducted at a rate of approximately 10%. Analysis of the replicate extractions yielded a mean relative percent difference (RPD) of 9.7% for TNT and 8.6% for RDX. Split analyses were conducted to evaluate instrument precision. The split analysis consisted of subsampling the extractant followed by analysis of each subsample. Split analyses were conducted at a rate of approximately 15%. Split analyses yielded a mean RPD of 20.7% for TNT and 19.0% for RDX. Additionally, matrix blank analyses were conducted to ensure that reagents used in the solid phase extraction process (acetonitrile and HPLC grade water) were free of constituents that would interfere with analysis of energetic compounds. Blank analysis was conducted at a rate of approximately 10%.

For the Phase 2 studies, replicate samples to evaluate batch and column variability were collected at a rate of 10%. Analysis of replicates indicated an RPD of approximately 2.8% for RDX and 8.0% for TNT. Instrument calibration checks were conducted during analysis runs every 10th sample. Results indicated a mean relative standard deviation of 0.35% for RDX and 1.7% for TNT.

Site Screening for Field Demonstration

Phase 2 work included a task to screen potential DoD sites for a field demonstration of e⁻barrier technology for treatment of energetic compounds in groundwater. Several sites were identified and investigated including Cornhusker AAP, Iowa AAP and the PCD. Discussions with DoD personnel at the PCD were initiated based on our preliminary screening criteria. A site visit was conducted to PCD on September 8, 2003 to tour the site and discuss site conditions and possible collaboration on a field demonstration. Site soils were also collected for preliminary geochemical evaluation and for use in preliminary treatability studies.

In general, the PCD appears to be the most favorable location for a field demonstration. Several screening attributes have been evaluated on a preliminary basis:

- RDX constituent of concern (approximately 500 ug/L)
- Depth of RDX plume approximately 20 ft bgs
- Saturated thickness approximately 6 ft
- Aquifer comprised of primarily sand- trace silt and trace gravel
- Significant plume characterization exists (Earth Tech)
- Hydraulic conductivity high (~10 ft/day) based on slug tests
- Groundwater monitoring network in place
- Downstream receptor (irrigation wells)
- e⁻barrier technology developed at PCD could replace an existing high cost pump and treat system

Additional site evaluation will be required prior to design and construction of the field demonstration e⁻barrier.

Preliminary treatability studies were conducted using a flow-through setup as described above and site soils collected during the visit to PCD. Results from the study suggest that high fractional removal of RDX and HMX is possible using e⁻barrier technology using a single electrode set (Figure 48).

In October, 2004 a proposal for a demonstration/validation project of e⁻barrier technology for treatment of RDX at PCD was accepted for funding by ESTCP. The project is scheduled for initiation in March, 2005.
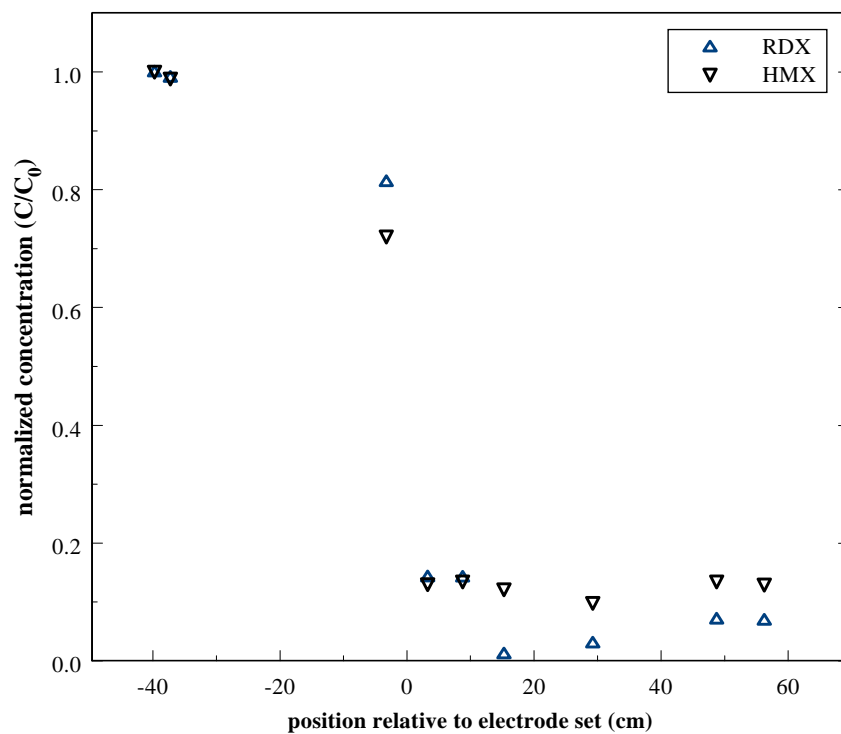
Figure 48. RDX and HMX Transformation as a Function of Position in the Column. The Electrode Set is at Position 0.

Conclusion

SERDP ER-1234 consisted of two research phases: proof-of concept level investigation and analysis of potential reaction pathways and reaction products.

The Phase 1 research included proof of concept experiments to evaluate the potential of using electrolytic barriers to reduce the risk associated with groundwater contaminated with energetic compounds. The results from this phase suggest that e⁻barriers are a promising option for treatment of energetic compounds in groundwater. Specifically, high fractional removal of TNT and RDX was observed with minimal generation of deleterious products at low power requirements.

The batch reactor experiments conducted in Phase 2 suggest that the high fractional TNT removal found during the proof of concept experiments can be explained by heterogeneous cathodic reduction of TNT. The rate of TNT transformation is dependent on applied potential. No transformation was observed at cell potentials below 2V. Significant formation of nitrite during the experiments suggests that loss of a nitro group from TNT occurs early in the transformation. The resultant pathway therefore may follow a DNT reductive path likely resulting in compounds of MW 98, 96 and 77. Additional studies have been initiated to better resolve this pathway, identify unknown products to quantify the identified products. Results using RDX indicated that heterogeneous cathodic reduction was also responsible for the high fractional removal observed during the Phase 1 experiments. Significant nitrite was formed and further reduced during the batch reactor experiments. At least one pathway has been identified involving formation of nitroso-substituted intermediates (MNX, DNX, and TNX) at low concentration. Other intermediates identified include nitramide.

Screening of sites for a future field demonstration for e⁻barrier technology to treat groundwater contaminated with energetic compounds has resulted in discussion with site personnel at the PCD (Pueblo, Colorado). A site visit was conducted and site soils and information were collected. Preliminary treatability studies indicated that high fractional RDX transformation can be achieved using e⁻barrier technology at PCD.

Based on the results of SERDP ER-1234, a proposal was accepted by ESTCP titled: Field Demonstration/ Validation of e⁻barrier technology for Treatment of Energetic Compounds in Groundwater: Pueblo Chemical Depot. The transition plan is to conduct a 2 year field demonstration under ESTCP funding followed by a full-scale e⁻barrier funded under Base Realignment and Closure (BRAC). The ESTCP project will provide cost and implementation information for those sites implementing e⁻barrier technology in the future.

Utility of the technology – Results from SERDP ER-1234 and complementary projects indicate that an electrolytic reactive barrier has wide applicability for treatment of groundwater containing dissolved organic contaminants.

Potential Economic Benefit – Laboratory and field studies indicate that operational power costs associated with the e⁻barrier are low ($0.10/day).   Primary cost drivers are electrode materials and installation.

Unresolved issues – Additional work is required to verify (and if necessary modify) the hypothesized reaction pathways, particularly among the low molecular weight products. This area is the focus of research among several groups in the scientific community. It is expected that understanding and verification of the full electrolytic transformation pathway will evolve over the next few years as new discoveries are made. The lack of identified reaction intermediates during the mass balance experiments and the limited identification of products of low molecular weight reflects this issue.

Technology transfer – To date, two manuscripts associated with ER-1234 have been prepared and submitted for peer review:

Sequential Electrolytic Transformation of Aqueous Energetic Compounds.   Gilbert, D.M., and Sale, T.C. 2004.

Electrolytic Transformation of Ordnance Related Compounds in Groundwater: Laboratory Mass Balance Studies. Wani, A. H., O'Neal, B.R., Gilbert, D.M. and Davis, J.L., 2004.

An additional manuscript is currently in preparation.

Several presentations covering this project have been made at conferences and workshops:

- American Geophysical Union – Hydrology Days, March 2002

- Partners in Environmental Technology, December 2002, December 2003

- Conference on Sustainable Range Management, January 2004

- Solvents in Groundwater Research Consortium Annual Meeting, May 2004

- U.S. Army Corps of Engineers Waterways Experiment Station, January 2004

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